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NEWS 1		Web Page for STN Seminar Schedule - N. America
NEWS 2	MAR 31	IFICDB, IFIPAT, and IFIUDB enhanced with new custom IPC display formats
NEWS 3	MAR 31	CAS REGISTRY enhanced with additional experimental spectra
NEWS 4	MAR 31	CA/CAplus and CASREACT patent number format for U.S. applications updated
NEWS 5	MAR 31	LPCI now available as a replacement to LDPCI
NEWS 6	MAR 31	EMBASE, EMBAL, and LEMBASE reloaded with enhancements
NEWS 7	APR 04	STN AnaVist, Version 1, to be discontinued
NEWS 8	APR 15	WPIDS, WPINDEX, and WPIX enhanced with new predefined hit display formats
NEWS 9	APR 28	EMBASE Controlled Term thesaurus enhanced
NEWS 10	APR 28	IMSRESEARCH reloaded with enhancements
NEWS 11	MAY 30	INPAFAMDB now available on STN for patent family searching
NEWS 12	MAY 30	DGENE, PCTGEN, and USGENE enhanced with new homology sequence search option
NEWS 13	JUN 06	EPFULL enhanced with 260,000 English abstracts
NEWS 14	JUN 06	KOREAPAT updated with 41,000 documents
NEWS 15	JUN 13	USPATFULL and USPAT2 updated with 11-character patent numbers for U.S. applications
NEWS 16	JUN 19	CAS REGISTRY includes selected substances from web-based collections
NEWS 17	JUN 25	CA/CAplus and USPAT databases updated with IPC reclassification data
NEWS 18	JUN 30	AEROSPACE enhanced with more than 1 million U.S. patent records
NEWS 19	JUN 30	EMBASE, EMBAL, and LEMBASE updated with additional options to display authors and affiliated organizations
NEWS 20	JUN 30	STN on the Web enhanced with new STN AnaVist Assistant and BLAST plug-in
NEWS 21	JUN 30	STN AnaVist enhanced with database content from EPFULL
NEWS 22	JUL 28	CA/CAplus patent coverage enhanced
NEWS 23	JUL 28	EPFULL enhanced with additional legal status information from the epoline Register
NEWS 24	JUL 28	IFICDB, IFIPAT, and IFIUDB reloaded with enhancements
NEWS 25	JUL 28	STN Viewer performance improved
NEWS 26	AUG 01	INPADOCDB and INPAFAMDB coverage enhanced

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 NEWS EXPRESS JUNE 27 08 CURRENT WINDOWS VERSION IS V8.3,
              AND CURRENT DISCOVER FILE IS DATED 23 JUNE 2008.

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FILE 'HOME' ENTERED AT 17:41:05 ON 05 AUG 2008

=> file reg
COST IN U.S. DOLLARS                                SINCE FILE      TOTAL
                                                         ENTRY    SESSION
FULL ESTIMATED COST                                       0.21       0.21

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DICTIONARY FILE UPDATES:   4 AUG 2008  HIGHEST RN 1038507-75-3

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Uploading C:\Program Files\Stnexp\Queries\10571261\Struc 1.str
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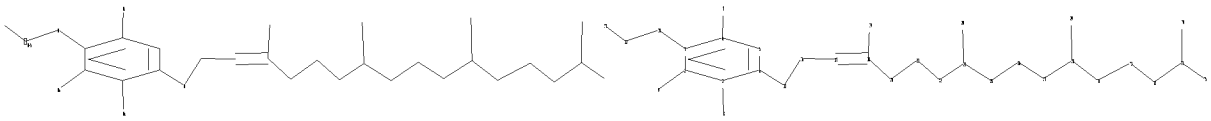

chain nodes :
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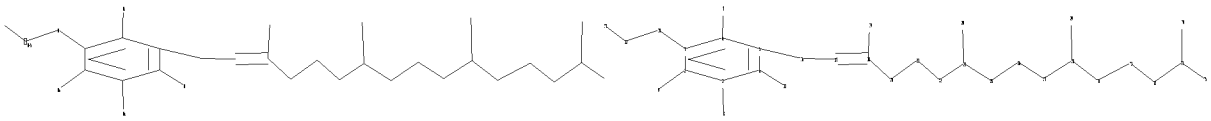
31 32 33 34 35
ring nodes :
1 2 3 4 5 6
chain bonds :
1-8 2-9 3-10 4-7 6-11 10-12 11-16 12-13 16-17 17-18 18-19 18-20 20-21
21-22 22-23 23-24 23-25 25-26 26-27 27-28 28-29 28-30 30-31 31-32 32-33
33-34 33-35
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6
exact/norm bonds :
3-10 6-11 10-12 11-16
exact bonds :
1-8 2-9 4-7 12-13 16-17 17-18 18-19 18-20 20-21 21-22 22-23 23-24 23-25
25-26 26-27 27-28 28-29 28-30 30-31 31-32 32-33 33-34 33-35
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS 8:CLASS 9:CLASS 10:CLASS
11:CLASS 12:CLASS 13:CLASS 16:CLASS 17:CLASS 18:CLASS 19:CLASS 20:CLASS
21:CLASS 22:CLASS 23:CLASS 24:CLASS 25:CLASS 26:CLASS 27:CLASS 28:CLASS
29:CLASS 30:CLASS 31:CLASS 32:CLASS 33:CLASS 34:CLASS 35:CLASS

L1 STRUCTURE UPLOADED

=>
Uploading C:\Program Files\Stnexp\Queries\10571261\Struc 2.str



chain nodes :
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ring nodes :
1 2 3 4 5 6
chain bonds :
1-8 2-9 3-10 4-7 5-16 6-11 10-12 12-13 16-17 17-18 18-19 18-20 20-21
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33-34 33-35
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6
exact/norm bonds :
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exact bonds :
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23-25 25-26 26-27 27-28 28-29 28-30 30-31 31-32 32-33 33-34 33-35
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:CLASS 8:CLASS 9:CLASS 10:CLASS
11:CLASS 12:CLASS 13:CLASS 16:CLASS 17:CLASS 18:CLASS 19:CLASS 20:CLASS
21:CLASS 22:CLASS 23:CLASS 24:CLASS 25:CLASS 26:CLASS 27:CLASS 28:CLASS
29:CLASS 30:CLASS 31:CLASS 32:CLASS 33:CLASS 34:CLASS 35:CLASS

L2 STRUCTURE UPLOADED

=> l1 or l2
SAMPLE SEARCH INITIATED 17:42:01 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 16 TO ITERATE

100.0% PROCESSED 16 ITERATIONS 0 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**

```
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS:           80 TO      560
PROJECTED ANSWERS:               0 TO        0

L3            0 SEA SSS SAM L1 OR L2

=> l1 or l2 full
FULL SEARCH INITIATED 17:42:05 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -      240 TO ITERATE

100.0% PROCESSED      240 ITERATIONS                              25 ANSWERS
SEARCH TIME: 00.00.01

L4           25 SEA SSS FUL L1 OR L2

=> file caplus
COST IN U.S. DOLLARS                              SINCE FILE      TOTAL
                                                      ENTRY    SESSION
FULL ESTIMATED COST                                  271.76     271.97

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FILE LAST UPDATED: 4 Aug 2008  (20080804/ED)

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=> l4
L5           19 L4

=> l5 and cross-methathesis
        562692 CROSS
           196 METHATHESIS
             6 CROSS-METHATHESIS
                 (CROSS(W)METHATHESIS)
L6           0 L5 AND CROSS-METHATHESIS
```

```
=> l5 and methathesis
           196 METHATHESIS
L7           0 L5 AND METHATHESIS

=> l5 and ruthenium
        104413 RUTHENIUM
L8           5 L5 AND RUTHENIUM

=> l5 and catalyst
        809697 CATALYST
L9           7 L5 AND CATALYST

=> l8 or l9
L10          8 L8 OR L9

=> d ibib abs hitstr 1-9

L10  ANSWER 1 OF 8  CAPLUS  COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER:        2007:188349  CAPLUS
DOCUMENT NUMBER:         146:441949
TITLE:                   A new route to Vitamin E key-intermediates by olefin
                         cross-metathesis
AUTHOR(S):               Netscher, Thomas; Malaise, Gregory; Bonrath, Werner;
                         Breuninger, Manfred
CORPORATE SOURCE:        Research and Development, DSM Nutritional Products,
                         Basel, CH-4002, Switz.
SOURCE:                  Catalysis Today (2007), 121(1-2), 71-75
                         CODEN: CATTEA; ISSN: 0920-5861
PUBLISHER:               Elsevier B.V.
DOCUMENT TYPE:           Journal
LANGUAGE:                English
OTHER SOURCE(S):         CASREACT 146:441949
GI
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* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Ruthenium-catalyzed olefin cross-metathesis of allylhydroquinone derivs. I [R = H, Me; R1 = H, Ac, Bu3Si, Me3CSi(Me)2] and allyloxyphenol acetates II (R2, R3 = H, Me) with olefins Me2CH(CH2)3CHMe(CH2)3CHMe(CH2)3CMe:CHR4 (R4 = H, OHCOCH2, AcOCH2, PhCOOCH2) in the presence of either the second generation Grubbs catalyst or the Hoveyda-Grubbs catalyst yields the alkenyl hydroquinone derivs. III [R1 = H, Ac, Bu3Si, Me3CSi(Me)2] and the allyloxyphenol acetate IV, resp., as mixts. of olefin diastereomers. Using nonracemic phytol or phytol acetate, I (R = Me; R1 = Ac) and II (R2 = R3 = Me) are converted to a mixture of α-tocopheryl acetate epimers (no data).

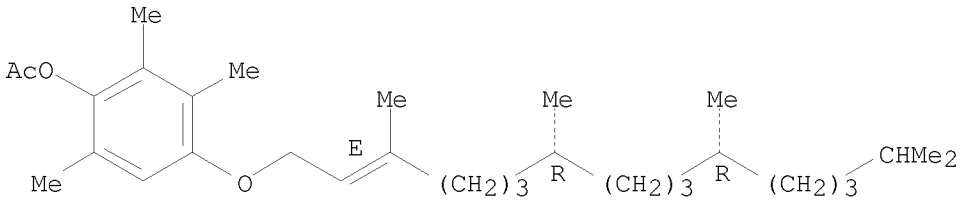
IT 696598-05-7P 928344-37-0P 928344-39-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of α-tocopheryl acetate epimers using ruthenium -catalyzed cross-metathesis reactions of allylhydroquinone derivs. and allylphenyl acetates with nonracemic phytol and phytol acetate)

RN 696598-05-7 CAPLUS

CN Phenol, 2,3,6-trimethyl-4-[[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-

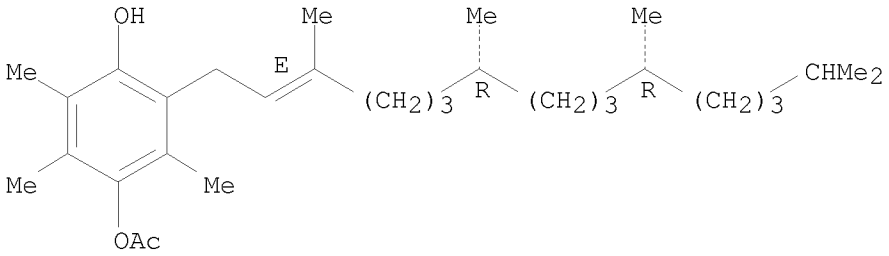
1-yl]oxy]-, 1-acetate (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.



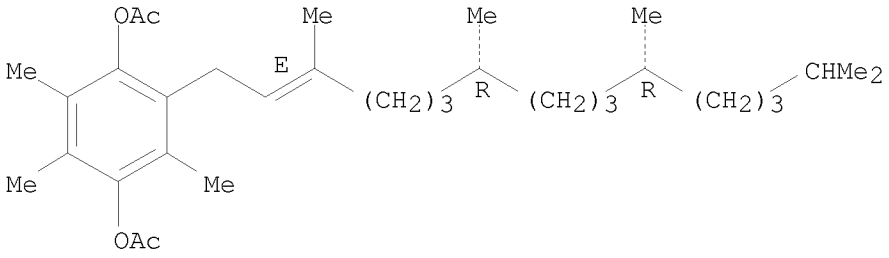
RN 928344-37-0 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 4-acetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.



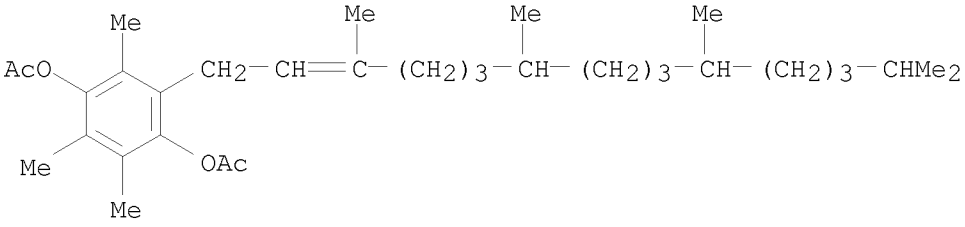
RN 928344-39-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 1,4-diacetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.

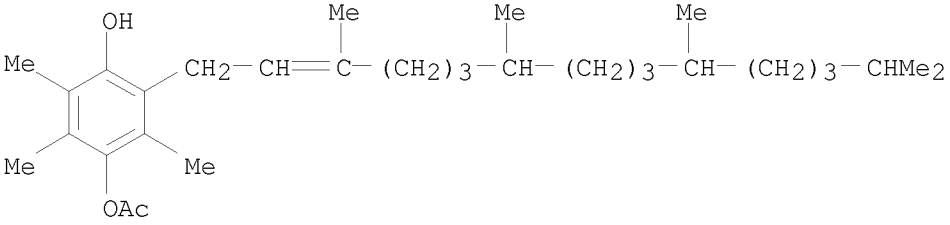


IT 85314-71-2
RL: RCT (Reactant); RACT (Reactant or reagent)
(stereoselective preparation of intermediates for the synthesis of Vitamin E acetate by ruthenium-catalyzed cross-metathesis reactions of allylhydroquinone derivs. with racemic phytol derivs.)
RN 85314-71-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-

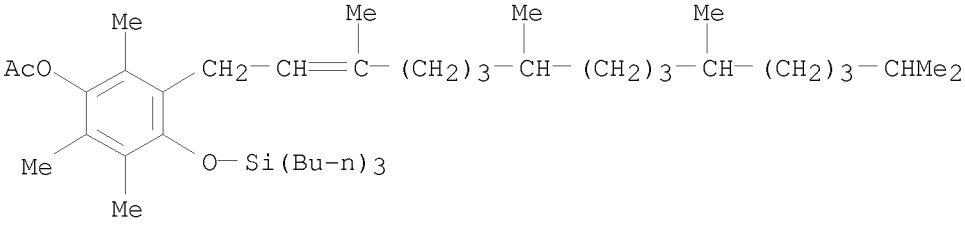
yl)-, 1,4-diacetate (CA INDEX NAME)



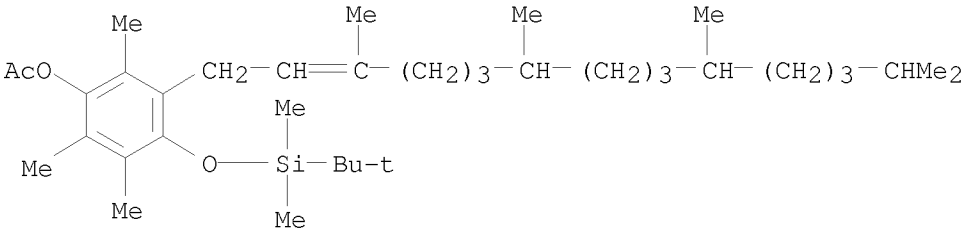
IT 728894-66-4P 892403-67-7P 892403-69-9P
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereoselective preparation of intermediates for the synthesis of Vitamin E acetate by ruthenium-catalyzed cross-metathesis reactions of allylhydroquinone derivs. with racemic phytol derivs.)
RN 728894-66-4 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 4-acetate (CA INDEX NAME)



RN 892403-67-7 CAPLUS
CN Phenol, 2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-4-[(tributylsilyl)oxy]-, 1-acetate (CA INDEX NAME)

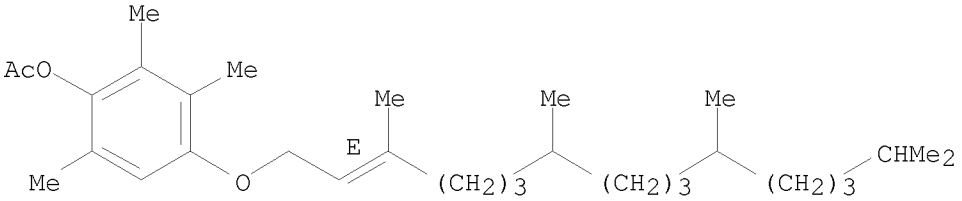


RN 892403-69-9 CAPLUS
CN Phenol, 4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1-acetate (CA INDEX NAME)



IT 928344-32-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(stereoselective preparation of intermediates for the synthesis of Vitamin E acetate by ruthenium-catalyzed cross-metathesis reactions of allylphenyl acetates with phytol derivs.)
RN 928344-32-5 CAPLUS
CN Phenol, 2,3,6-trimethyl-4-[[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate (CA INDEX NAME)

Double bond geometry as shown.



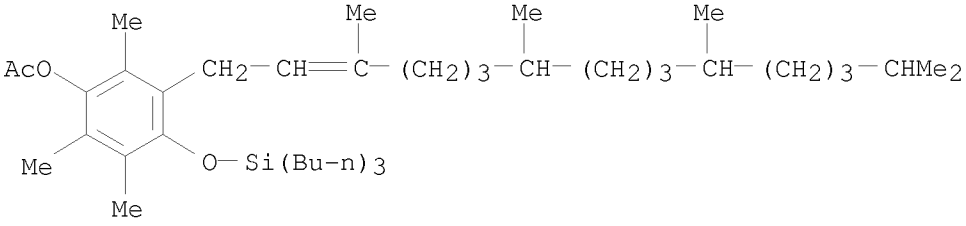
REFERENCE COUNT: 55 THERE ARE 55 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 2 OF 8 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2006:448874 CAPLUS
DOCUMENT NUMBER: 145:82978
TITLE: A new route to vitamin E key-intermediates by olefin cross-metathesis
AUTHOR(S): Malaise, Gregory; Bonrath, Werner; Breuninger, Manfred; Netscher, Thomas
CORPORATE SOURCE: Research and Development, Basel, CH-4002, Switz.
SOURCE: Helvetica Chimica Acta (2006), 89(4), 797-812
CODEN: HCACAV; ISSN: 0018-019X
PUBLISHER: Verlag Helvetica Chimica Acta
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 145:82978
AB Ruthenium-catalyzed olefin cross-metathesis (CM) of phytyl functional derivs. with allyl-substituted hydroquinone esters gave 3,7,11,15-tetramethyl-2-hexadecenylhydroquinone derivs. with a trisubstituted C:C bond, as useful intermediates for an alternative route to α-tocopherol acetate (vitamin E acetate). Using the second-generation Grubbs catalyst RuCl2(SIMes)(:CHPh)PCy3 (4a, SIMes = 1,3-dimesitylimidazolidin-2-ylidene, Cy = cyclohexyl) and Hoveyda-Grubbs catalyst [RuCl2(SIMes)[:CHC6H4(iPrO-κO)-2]] (4b), the metathesis of C3-allyl hydroquinones 1-AcO-2,5,6-Me3-4-

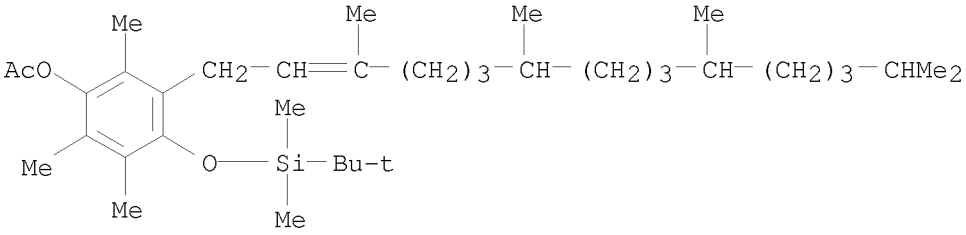
OR3C6CH2CH:CR22-3 (5a-f; R2, R3: H, H; H, Ac; Me, H; Me, Ac; Me, Bu3Si; Me, tBuMe2Si) with phytyl derivs. R4CH:CMe(CH2)3CHMe(CH2)3CHMe(CH2)3CHMe2 (6a-f; R4 = H, HOCH2, OHCOCH2, AcOCH2, PhCO2CH2, OHC) gave the corresponding 1-AcO-2,5,6-Me3-4-OR3C6CH2CH:CMe(CH2)3CHMe(CH2)3CHMe(CH2)3CHMe2 (2b,d-f; R3 = H, Ac, Bu3Si, tBuMe2Si); the product 2b (R3 = H) may be cyclized to α-tocopherol acetate. 1-Acetoxy-2,3,6-trimethyl-4-phytyloxybenzene hydroquinone [3b, phytyl = CH2CH:CMe(CH2)3CHMe(CH2)3CHMe(CH2)3CHMe2] were prepared analogously from O-allyl 2,3,6-trimethylhydroquinone acetates. The vitamin E precursors could be prepared in up to 83% isolated yield as (E/Z)-mixts.

IT 892403-67-7P 892403-69-9P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of vitamin E intermediates, phytyl hydroquinone derivs. by cross-metathesis of allylhydroquinones with tetramethylhexadecenyl esters and aldehyde)

RN 892403-67-7 CAPLUS
CN Phenol, 2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-4-[(tributylsilyl)oxy]-, 1-acetate (CA INDEX NAME)

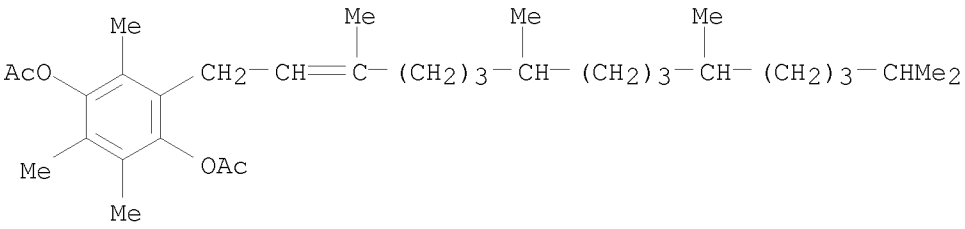


RN 892403-69-9 CAPLUS
CN Phenol, 4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1-acetate (CA INDEX NAME)

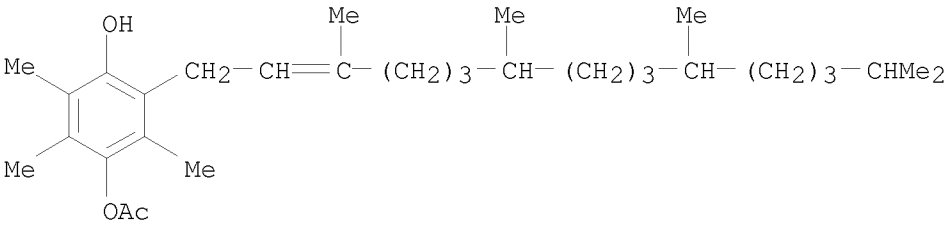


IT 85314-71-2P 728894-66-4P 892403-66-6P
892403-71-3P 900149-07-7P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of vitamin E intermediates, phytyl hydroquinone derivs. by cross-metathesis of allylhydroquinones with tetramethylhexadecenyl esters and aldehyde)

RN 85314-71-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)

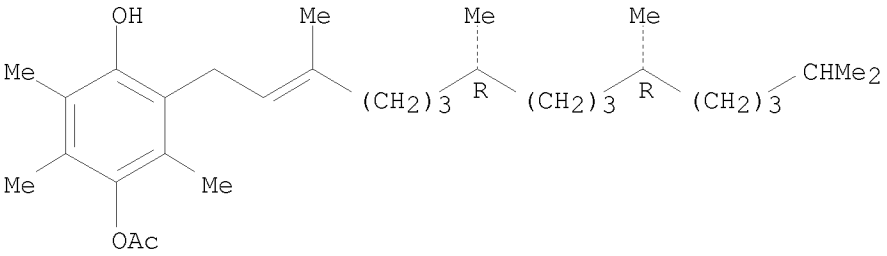


RN 728894-66-4 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 4-acetate (CA INDEX NAME)

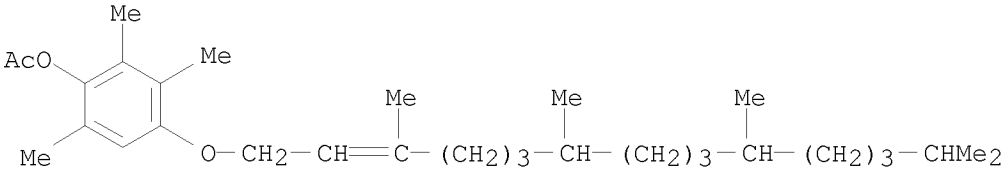


RN 892403-66-6 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 4-acetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry unknown.



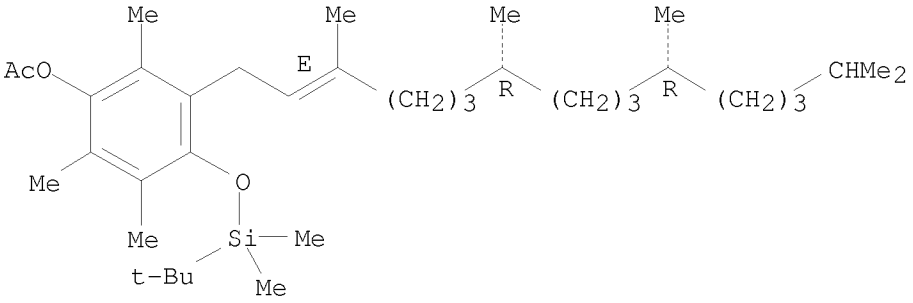
RN 892403-71-3 CAPLUS
CN Phenol, 2,3,6-trimethyl-4-[(3,7,11,15-tetramethyl-2-hexadecen-1-yl)oxy]-, 1-acetate (CA INDEX NAME)



RN 900149-07-7 CAPLUS

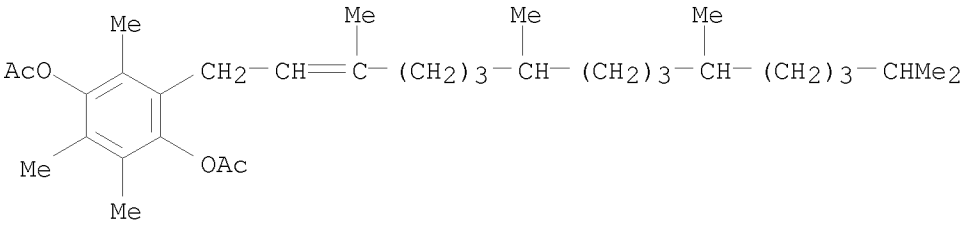
CN Phenol, 4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2,3,6-trimethyl-5-[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 1-acetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.



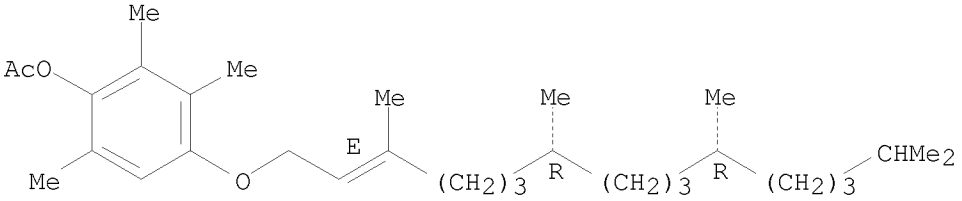
REFERENCE COUNT: 68 THERE ARE 68 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 3 OF 8 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2006:219352 CAPLUS
DOCUMENT NUMBER: 146:317055
TITLE: Olefin cross-metathesis in natural product synthesis: preparation of trisubstituted olefins on the way to vitamin E
AUTHOR(S): Netscher, Thomas; Malaise, Gregory; Bonrath, Werner; Breuninger, Manfred
CORPORATE SOURCE: Research and Development, DSM Nutritional Products, Basel, CH-4002, Switz.
SOURCE: Actualite Chimique (2006), 293, 21-23
CODEN: ACCHDG; ISSN: 0151-9093
PUBLISHER: Societe Francaise de Chimie
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 146:317055
AB The application of ruthenium catalyzed olefin cross-metathesis towards the synthesis of tocopherols (vitamin E) is described. This group of biol. most important fat-soluble antioxidants is synthetically available by various routes, for which key-intermediates containing trialkyl-substituted olefinic double bonds can now be prepared efficiently. The results presented may be of interest for the area of syntheses of isoprenoid natural products in general.
IT 85314-71-2P 696598-05-7P 728894-66-4P
892403-67-7P 892403-69-9P 928344-32-5P
928344-37-0P 928344-39-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of olefins as vitamin E precursors by cross-metathesis)
RN 85314-71-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)

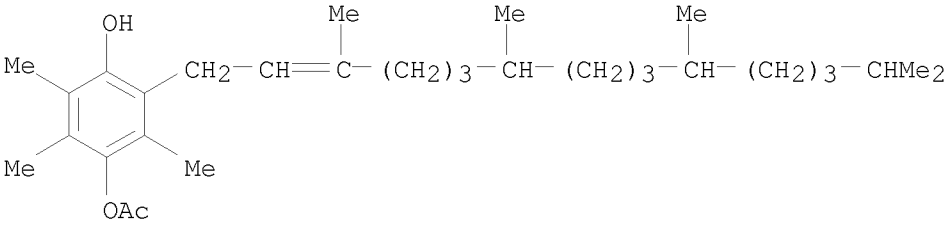


RN 696598-05-7 CAPLUS
CN Phenol, 2,3,6-trimethyl-4-[[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate (CA INDEX NAME)

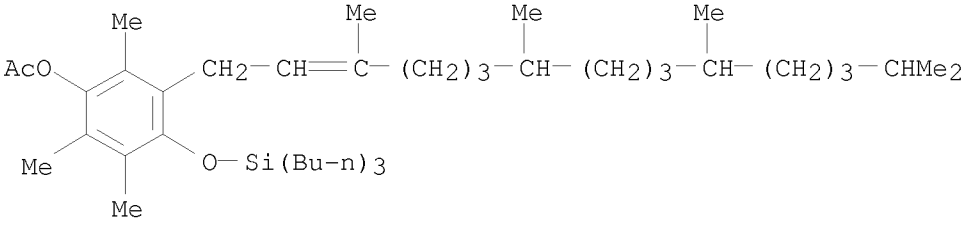
Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.



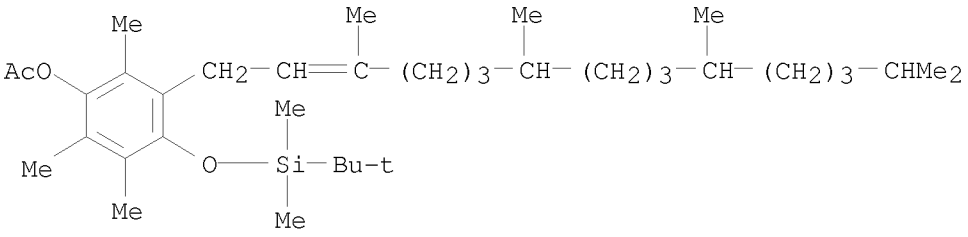
RN 728894-66-4 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 4-acetate (CA INDEX NAME)



RN 892403-67-7 CAPLUS
CN Phenol, 2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-4-[(tributylsilyl)oxy]-, 1-acetate (CA INDEX NAME)

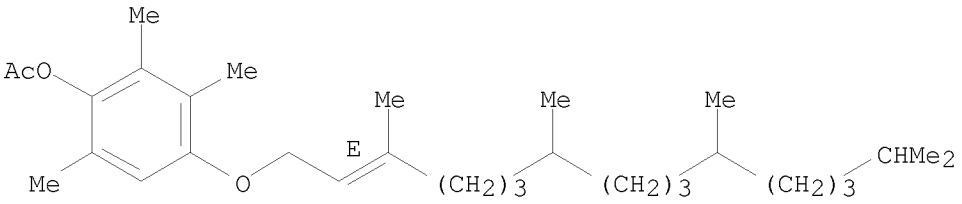


RN 892403-69-9 CAPLUS
CN Phenol, 4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1-acetate (CA INDEX NAME)



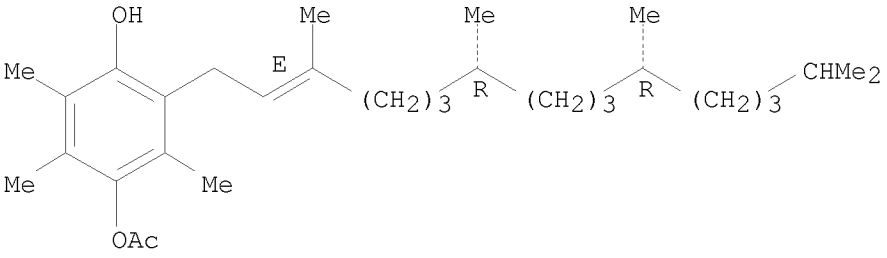
RN 928344-32-5 CAPLUS
CN Phenol, 2,3,6-trimethyl-4-[[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate (CA INDEX NAME)

Double bond geometry as shown.



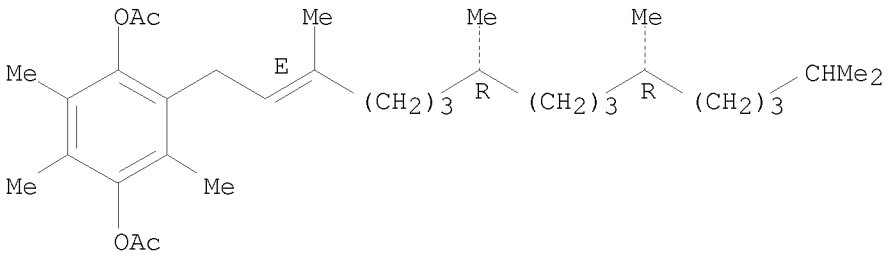
RN 928344-37-0 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 4-acetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.



RN 928344-39-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 1,4-diacetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.

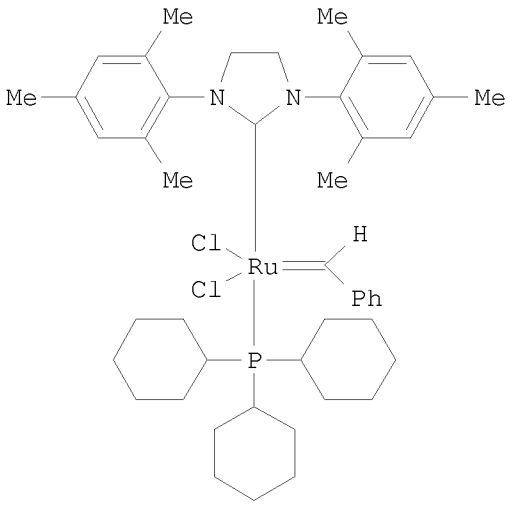


REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L10 ANSWER 4 OF 8 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2005:260080 CAPLUS
DOCUMENT NUMBER: 142:336488
TITLE: A new route to α-tocopherol, α-tocopheryl alkanoates and precursors
INVENTOR(S): Bonrath, Werner; Breuninger, Manfred; Malaise, Gregory; Netscher, Thomas
PATENT ASSIGNEE(S): DSM IP Assets B.V., Neth.
SOURCE: PCT Int. Appl., 37 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005026181	A2	20050324	WO 2004-EP9748	20040902
WO 2005026181	A3	20050707		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1664067	A2	20060607	EP 2004-786906	20040902
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK				
US 20060235234	A1	20061019	US 2006-571252	20060413
PRIORITY APPLN. INFO.:			EP 2003-20873 A	20030915
			WO 2004-EP9748 W	20040902

OTHER SOURCE(S): CASREACT 142:336488; MARPAT 142:336488
GI



II

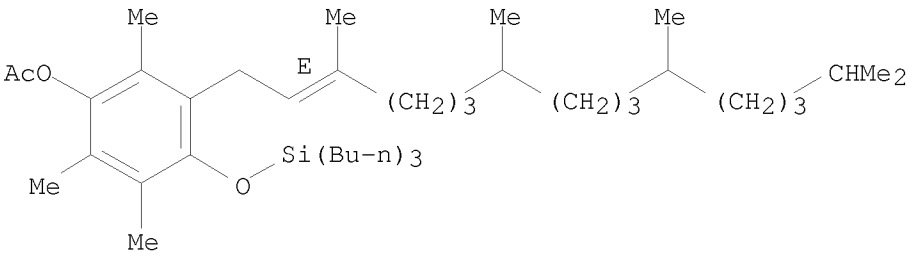
AB The present invention is concerned with a novel process for the manufacture of (E/Z)-4-alkanoyloxy-3,5,6-trimethyl-2-phytylphenyl esters and silyl ethers, precursors of α- tocopherol and α-tocopheryl alkanoates, by the cross-metathesis reaction of 2-alkenyl-3,5,6-trimethylhydroquinone dialkanoates or 4-alkanoyloxy-2-alkenyl-3,5,6-trimethylphenyl silyl ethers with 2,6,10,14-tetramethylpentadecene (I) or a phytol derivative, e.g. phytyl acetate, in the presence of a cross-metathesis catalyst. As the cross-metathesis catalyst, ruthenium metal carbene complexes which possess a ruthenium metal center and that have an electron count of 16 or 18 and are penta- or hexa-coordinated are especially suitable. For example, I was reacted with 3-(3'-methyl-2'-butenyl)-2,5,6-trimethylhydroquinone diacetate to give (E/Z)-3-phytyl-2,5,6-trimethylhydroquinone diacetate in 69% yield using ruthenium catalyst II. A main objective of this invention is to provide a method for the manufacture of α-tocopherol and α-tocopheryl alkanoates utilizing this reaction.

IT 848362-81-2P 848362-83-4P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of alkanoyloxyphytyl esters and silyl ethers as precursors of α-tocopherol and α-tocopheryl alkanoates via ruthenium-catalyzed cross-metathesis)

RN 848362-81-2 CAPLUS

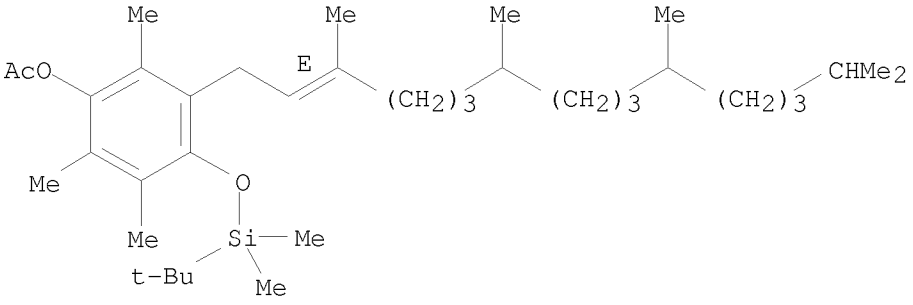
CN Phenol, 2,3,6-trimethyl-5-[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-4-[(tributylsilyl)oxy]-, 1-acetate (CA INDEX NAME)

Double bond geometry as shown.



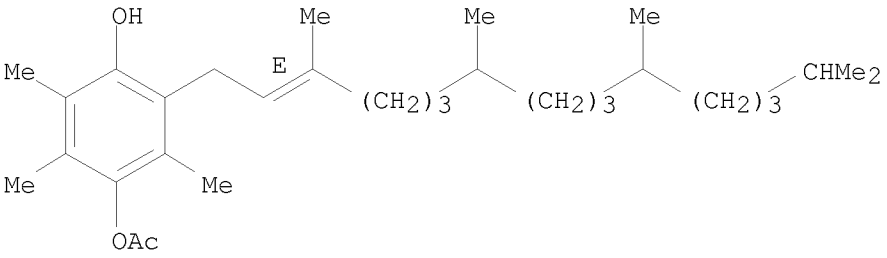
RN 848362-83-4 CAPLUS
CN Phenol, 4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2,3,6-trimethyl-5-[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 1-acetate (CA INDEX NAME)

Double bond geometry as shown.



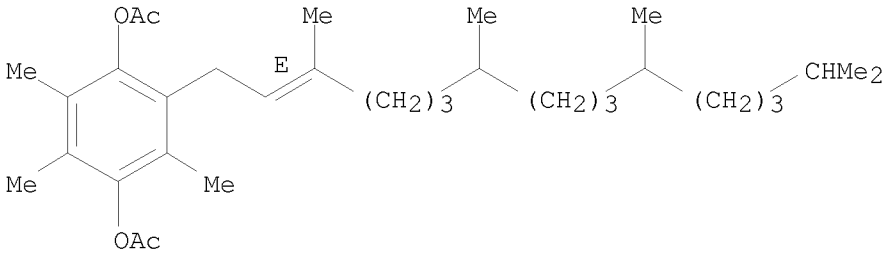
IT 696597-89-4P 848362-79-8P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(preparation of alkanoyloxyphytyl esters and silyl ethers as precursors of α-tocopherol and α-tocopheryl alkanoates via ruthenium-catalyzed cross-metathesis)
RN 696597-89-4 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 4-acetate (CA INDEX NAME)

Double bond geometry as shown.



RN 848362-79-8 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 1,4-diacetate (CA INDEX NAME)

Double bond geometry as shown.



L10 ANSWER 5 OF 8 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2005:260046 CAPLUS
DOCUMENT NUMBER: 142:336487
TITLE: A new route to α-tocopheryl alkanoates and percursors thereof
INVENTOR(S): Bonrath, Werner; Breuninger, Manfred; Malaise, Gregory; Netscher, Thomas
PATENT ASSIGNEE(S): DSM IP Assets B.V., Neth.
SOURCE: PCT Int. Appl., 36 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005026142	A2	20050324	WO 2004-EP9749	20040902
WO 2005026142	A3	20050609		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1663937	A2	20060607	EP 2004-764709	20040902
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK				
US 20070032667	A1	20070208	US 2006-571261	20060413

PRIORITY APPLN. INFO.:		EP 2003-20875	A 20030915
		WO 2004-EP9749	W 20040902

OTHER SOURCE(S): CASREACT 142:336487; MARPAT 142:336487
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

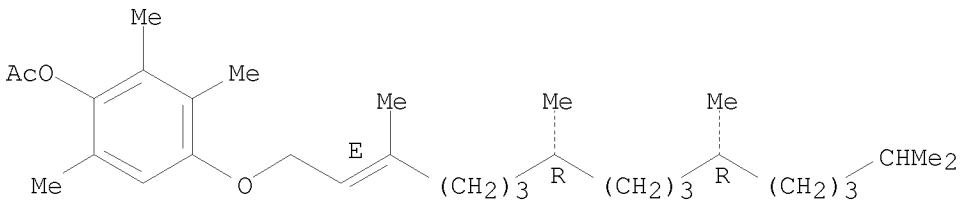
AB The present invention is concerned with a novel process for the manufacture of 4-alkanoyloxy-2,3,5-trimethylphenyl (E/Z)-phytyl ethers I, precursors of α-tocopheryl alkanoates II, by cross-metathesis reaction of alkenyl ethers III (R1, R2 = H, C1-5-alkyl, with the proviso that at least one of R1 and R2 ≠ H; R3 = C2-5-alkanoyloxy) of 1-alkanoyl-2,3,6-trimethylhydroquinone with 2,6,10,14-tetramethylpentadecene, R4CH:CMe(CH2CH2CH2CHMe)3Me [R4 = H, CH2R5; R5 = OCHO, C2-5-alkanoyloxy, O2CPh, C1-5-alkoxy, OSiR6R7R8; R6, R7, R8 = C1-6-alkyl, Ph] or a phytol derivative, e.g. an ester, an ether or a silyl ether, in the presence of a cross-metathesis catalyst. As the cross metathesis catalyst especially ruthenium metal carbene complexes, e.g., A:RuCl2LL1 [A = CH2, CH-aryl, CHR13, C:C(R13)2, C:CHSi(R14)3, CHCHC(R13)2, C:CHPh, CHCH:CPh2, C:C:CPh2 (aryl = optionally mono- or multiply-substituted C1-5-alkylated or halogenated Ph); G = ethane-1,2-diyl, ethylene-1,2-diyl, cyclohexane-1,2-diyl, 1,2-diphenylethane-1,2-diyl; R9 = ; L1 = PR10R11R12; R10, R11, R12 = C1-8-alkyl, Ph, C6H4Me; R13 = C1-4-alkyl; R14 = C1-6-alkyl, Ph], A:RuCL2L2L3L4 [L2 = L, L1; L3, L4 = pyridyl, 3-bromopyridyl, 3-chloropyridyl], IV [R15, R16 = H; R15R16 = fused benzene ring; R17 = C1-5-alkyl], are suitable which possess (a) ruthenium metal center(s), have an electron count of 16 or 18 and are penta- or hexa-coordinated. Thus, (±)-(2E/Z,7R,11R)-I was prepared from 2,3,6-trimethylhydroquinone via O-alkylation with dimethyllallyl bromide in THF containing NaH and cross-metathesis with 2,6,10,14-tetramethylpentadecene in PhMe/Me(CH2)11Me containing a catalytic Grubb's ruthenium catalyst type 2 [benzylidenedichloro(N,N-dimesityltetrahydroimidazol-2-yl)(tricyclohexylphosphine)ruthenium]. A further object of the invention is a process for the manufacture of α-tocopheryl alkanoates comprising this reaction.

IT 696598-05-7P, 4-Acetoxy-2,3,5-trimethylphenyl (E,R,R)-phytyl ether
848442-08-0P
RL: SPN (Synthetic preparation); PREP (Preparation)
(new route to α-tocopheryl alkanoates and percursors thereof via a cross-metathesis)

RN 696598-05-7 CAPLUS

CN Phenol, 2,3,6-trimethyl-4-[[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.

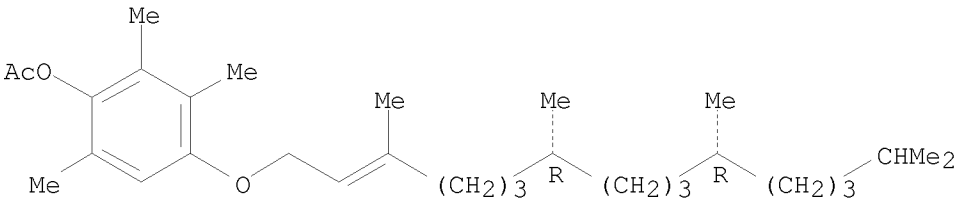


RN 848442-08-0 CAPLUS

CN Phenol, 2,3,6-trimethyl-4-[[(7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate, rel- (CA INDEX NAME)

Relative stereochemistry.

Double bond geometry unknown.

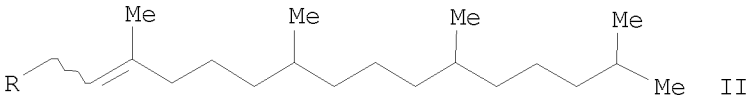


L10 ANSWER 6 OF 8 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2004:610127 CAPLUS
DOCUMENT NUMBER: 141:157318
TITLE: Manufacture of α-tocopheryl acetate from the reaction of 2,3,6-trimethylhydroquinone-1-acetate with phytol, iso-phytol or their derivatives in the presence of metal or rare earth metal triflate
INVENTOR(S): Bonrath, Werner; Dittel, Claus; Netscher, Thomas; Pabst, Thomas; Giraudi, Lisa
PATENT ASSIGNEE(S): DSM IP Assets B.V., Neth.
SOURCE: PCT Int. Appl., 21 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

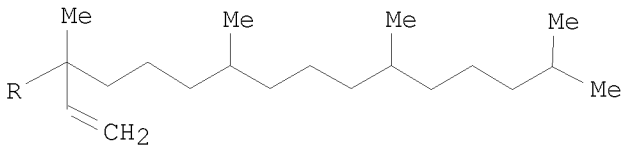
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004063182	A1	20040729	WO 2003-EP14723	20031222
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2003296706	A1	20040810	AU 2003-296706	20031222
EP 1583753	A1	20051012	EP 2003-815069	20031222
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
CN 1738810	A	20060222	CN 2003-80108718	20031222
JP 2006514959	T	20060518	JP 2004-566017	20031222
US 20060052618	A1	20060309	US 2005-541360	20050706
US 7135580	B2	20061114		

PRIORITY APPLN. INFO.:
EP 2003-493 A 20030113
EP 2003-24288 A 20031023
EP 2003-2488 A 20031023
WO 2003-EP14723 W 20031222

OTHER SOURCE(S): CASREACT 141:157318; MARPAT 141:157318
GI



II



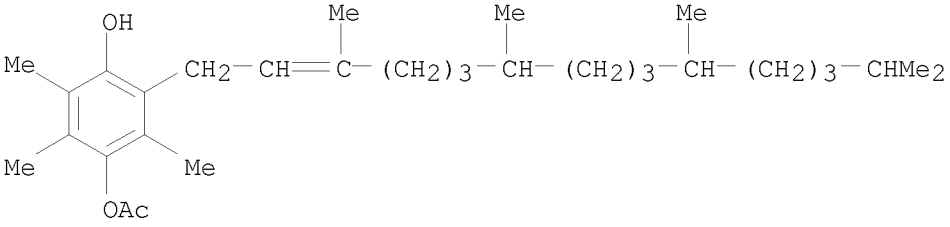
III

AB The present invention discloses a process for the manufacture of α-tocopheryl acetate (I) by reacting 2,3,6-trimethylhydroquinone-1-acetate with phytol (II; R = OH), iso-phytol (III; R = OH), and their derivs. (R = C2-to C5-alkanoyloxy, benzoyloxy, mesyloxy, benzenesulfonyloxy, tosyloxy) in the presence of a catalyst of the formula Mn+(R1SO3-)n, wherein Mn+= Ag, Cu, Ga, Hf, rare earth metal cation; n = valence of the cation Mn+; R1 = fluorine, C1-8-perfluoroalkyl or perfluoroaryl, and, if required, cyclizing any 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate or a double bond isomer thereof obtained as an intermediate reaction product, to produce I. In the catalyst Mn+ is preferably Ag+, Cu+, Ga3+, Sc3+, Lu3+, Ho3+, Tm3+, Yb3+ or Hf4+.

IT 728894-66-4P, 3-Phytyl-2,5,6-trimethylhydroquinone-1-acetate
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of α-tocopheryl acetate from the reaction of trimethylhydroquinone acetate and phytol, iso-phytol or their derivs. in the presence of metal or rare earth metal triflate)

RN 728894-66-4 CAPLUS

CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 4-acetate (CA INDEX NAME)



L10 ANSWER 7 OF 8 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2004:453199 CAPLUS
DOCUMENT NUMBER: 141:7308
TITLE: Manufacture of tocopheryl acetate
INVENTOR(S): Bonrath, Werner; Dittel, Claus; Netscher, Thomas; Pabst, Thomas; Schmid, Rudolf

PATENT ASSIGNEE(S): DSM IP Assets B.V., Neth.
SOURCE: PCT Int. Appl., 26 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004046126	A1	20040603	WO 2003-EP10789	20030929
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RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2003271655	A1	20040615	AU 2003-271655	20030929
EP 1562929	A1	20050817	EP 2003-753473	20030929
EP 1562929	B1	20071114		
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CN 1701066	A	20051123	CN 2003-825343	20030929
JP 2006515280	T	20060525	JP 2004-552466	20030929
AT 378325	T	20071115	AT 2003-753473	20030929
US 20060094886	A1	20060504	US 2005-535604	20050519
US 7169943	B2	20070130		
US 20070112206	A1	20070517	US 2006-639029	20061213

PRIORITY APPLN. INFO.: EP 2002-25989 A 20021121
WO 2003-EP10789 W 20030929
US 2005-535604 A3 20050519

OTHER SOURCE(S): CASREACT 141:7308; MARPAT 141:7308

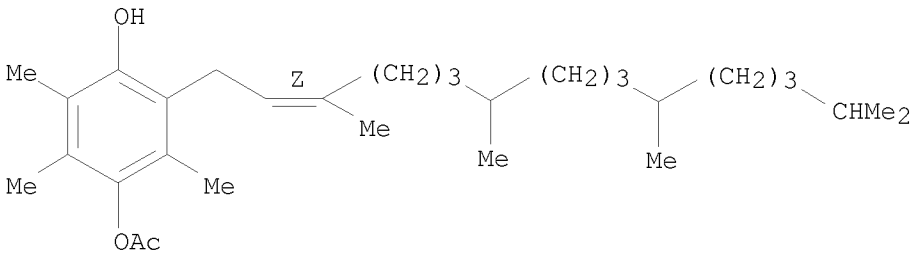
AB A process for the manufacture of 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate, and optionally tocopheryl acetate, by either C-alkylating 2,3,6-trimethylhydroquinone-1-acetate with isophytol or phytol in the presence of a sulfur(VI) containing catalyst of the formula R1SO2OH (R1 = hydroxy, halogen, lower alkyl, halogenated lower alkyl or aryl) in an aprotic organic solvent, or O-alkylating 2,3,6-trimethylhydroquinone-1-acetate with a phytyl halide in a polar aprotic organic solvent in the presence of a base, and subjecting the so-obtained 4-O-phytyl-2,3,6-trimethylhydroquinone-1-acetate to a rearrangement reaction, and in each case optionally submitting the so-obtained 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate to a ring closure reaction to produce tocopheryl acetate. The invention also includes the novel compound 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate and certain stereoisomers thereof, and also the further novel compound 4-hydroxy-2,3,6-trimethyl-5-[3-(4,8,12-trimethyltridecyl)-but-3-enyl]phenyl acetate which itself is one of several isomers of 3-phytyl-2,5,6-trimethylhydroquinone-1-acetate formed by isomerization under the influence of heating, e.g. during its distillation as part of the isolation and purification procedure following its manufacture as indicated above. (All-rac)-α -tocopherol, which may be derived from its acetate, is known to be the most active industrially important

member of the vitamin E group.

IT 696597-83-8P 696597-89-4P
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(manufacture of tocopheryl acetate by C-alkylation of 2,3,6-trimethylhydroquinone-1-acetate with isophytol or phytol in the presence of a sulfur(VI) containing catalyst)

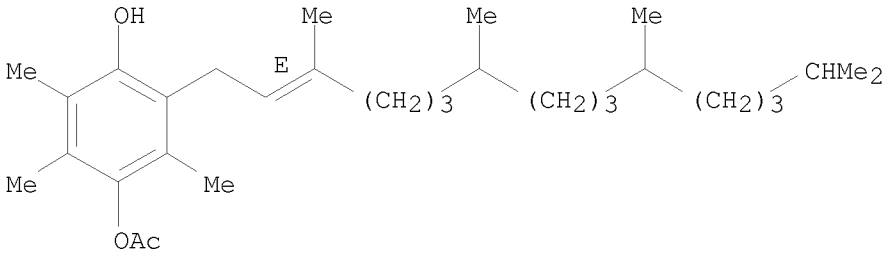
RN 696597-83-8 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2Z)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 4-acetate (CA INDEX NAME)

Double bond geometry as shown.



RN 696597-89-4 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 4-acetate (CA INDEX NAME)

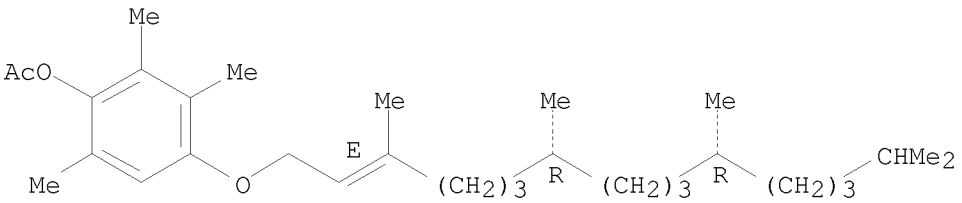
Double bond geometry as shown.



IT 696598-05-7P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(manufacture of tocopheryl acetate by C-alkylation of 2,3,6-trimethylhydroquinone-1-acetate with isophytol or phytol in the presence of a sulfur(VI) containing catalyst)

RN 696598-05-7 CAPLUS
CN Phenol, 2,3,6-trimethyl-4-[[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.



L10 ANSWER 8 OF 8 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2003:356435 CAPLUS
DOCUMENT NUMBER: 138:354126
TITLE: Manufacture of (all-rac)-α-tocopherol via acid-catalyzed ring closure
INVENTOR(S): Bonrath, Werner; Burdick, David Carl; Netscher, Thomas; Schager, Frank; Thomas, Dominik
PATENT ASSIGNEE(S): Roche Vitamins A.-G., Switz.
SOURCE: PCT Int. Appl., 20 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2003037883	A1	20030508	WO 2002-EP11819	20021023
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RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1446398	A1	20040818	EP 2002-785282	20021023
EP 1446398	B1	20050413		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK				
CN 1578777	A	20050209	CN 2002-821423	20021023
JP 2005507422	T	20050317	JP 2003-540164	20021023
AT 293108	T	20050415	AT 2002-785282	20021023
ES 2239260	T3	20050916	ES 2002-785282	20021023
US 20050187393	A1	20050825	US 2005-494005	20050426
PRIORITY APPLN. INFO.:			EP 2001-125966 A	20011031
			WO 2002-EP11819 W	20021023

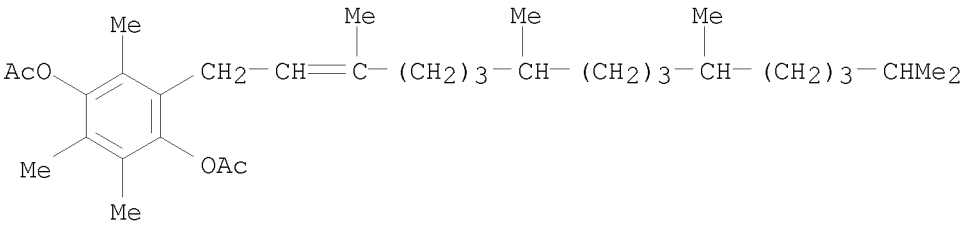
OTHER SOURCE(S): CASREACT 138:354126
AB A process for the manufacture of (all-rac)-α-tocopherol comprises submitting isolated, purified phytyltrimethylhydroquinone to acid catalysis, thereby promoting ring closure to (all-rac)-α-tocopherol. The process can be conducted in the absence or presence of an added solvent, and when a solvent or solvent mixture is used the solvent or at least one solvent component of the solvent mixture is preferably one with a

dipole moment greater than 9 x 10-30 C-m (or 2.7 D). The nature of the catalyst is immaterial, but the catalyst is preferably sulfuric acid, phosphoric acid, a polyperfluoroalkylenesulfonic acid, a 'NH-acid', a heteropoly acid, zinc chloride, boron trifluoride, aluminum trichloride, or a mixture of any of the aforementioned Broensted acids with any of the aforementioned Lewis acids. The product of the process is the most active an industrially most important member of the vitamin E group. Thus, phytyltrimethylhydroquinone in propylene carbonate and sulfuric acid in heptane were refluxed at 100°C for 1 h to give (all-rac)-α-tocopherol in 98.1% yield.

IT 85314-71-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of (all-rac)-α-tocopherol via acid-catalyzed ring closure)

RN 85314-71-2 CAPLUS

CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> l5 not l9
L11 12 L5 NOT L9

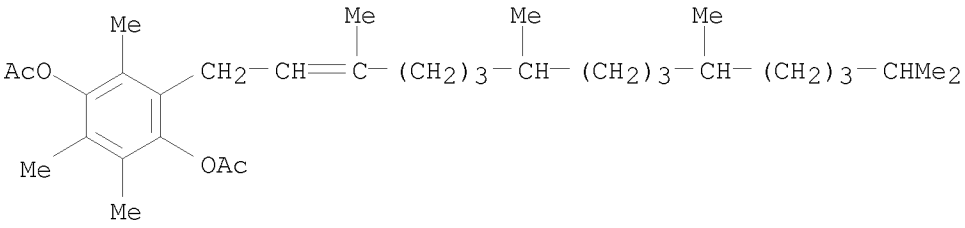
=> d ibib abs hitstr 1-12

L11 ANSWER 1 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2006:219352 CAPLUS
DOCUMENT NUMBER: 146:317055
TITLE: Olefin cross-metathesis in natural product synthesis: preparation of trisubstituted olefins on the way to vitamin E
AUTHOR(S): Netscher, Thomas; Malaise, Gregory; Bonrath, Werner; Breuninger, Manfred
CORPORATE SOURCE: Research and Development, DSM Nutritional Products, Basel, CH-4002, Switz.
SOURCE: Actualite Chimique (2006), 293, 21-23
CODEN: ACCHDG; ISSN: 0151-9093
PUBLISHER: Societe Francaise de Chimie
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 146:317055
AB The application of ruthenium catalyzed olefin cross-metathesis towards the synthesis of tocopherols (vitamin E) is described. This group of biol. most important fat-soluble antioxidants is synthetically available by various

routes, for which key-intermediates containing trialkyl-substituted olefinic double bonds can now be prepared efficiently. The results presented may be of interest for the area of syntheses of isoprenoid natural products in general.

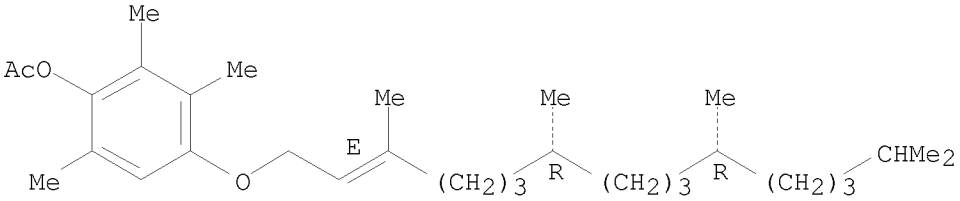
IT 85314-71-2P 696598-05-7P 728894-66-4P
892403-67-7P 892403-69-9P 928344-32-5P
928344-37-0P 928344-39-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of olefins as vitamin E precursors by cross-metathesis)

RN 85314-71-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)

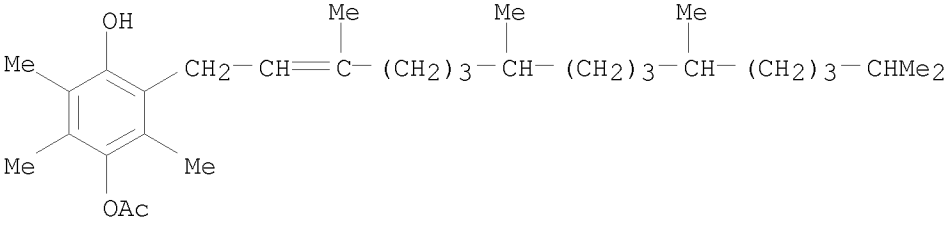


RN 696598-05-7 CAPLUS
CN Phenol, 2,3,6-trimethyl-4-[[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.

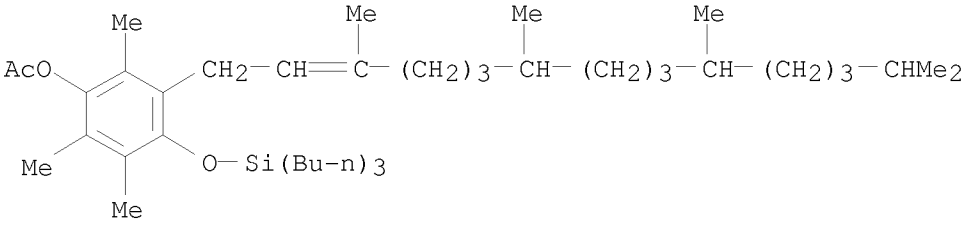


RN 728894-66-4 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 4-acetate (CA INDEX NAME)

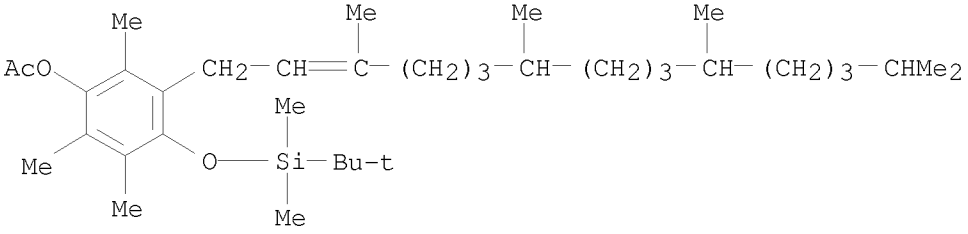


RN 892403-67-7 CAPLUS
CN Phenol, 2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-4-

[(tributylsilyl)oxy]-, 1-acetate (CA INDEX NAME)

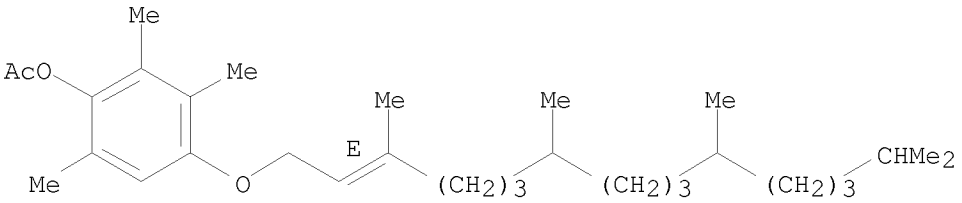


RN 892403-69-9 CAPLUS
CN Phenol, 4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2,3,6-trimethyl-5-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1-acetate (CA INDEX NAME)



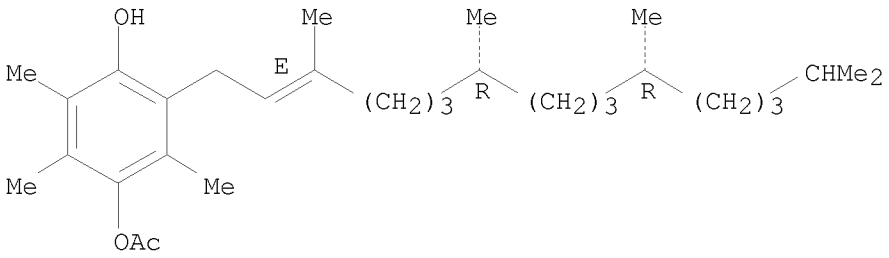
RN 928344-32-5 CAPLUS
CN Phenol, 2,3,6-trimethyl-4-[[(2E)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]oxy]-, 1-acetate (CA INDEX NAME)

Double bond geometry as shown.



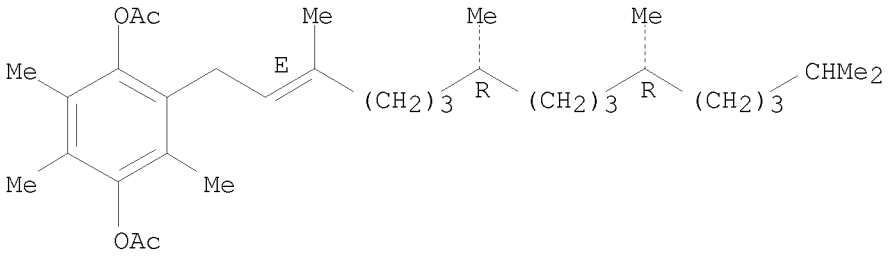
RN 928344-37-0 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 4-acetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.



RN 928344-39-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-[(2E,7R,11R)-3,7,11,15-tetramethyl-2-hexadecen-1-yl]-, 1,4-diacetate (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.



REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 2 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2004:618733 CAPLUS
DOCUMENT NUMBER: 141:174332
TITLE: Preparation of tocopherols, tocotrienols, other chroman and side chain derivatives for therapeutic use in the prevention and treatment of cancer
INVENTOR(S): Sanders, Bob G.; Kline, Kimberly; Hurley, Laurence; Gardner, Robb; Menchaca, Marla; Yu, Weiping; Ramanan, Puthucode N.; Liu, Shenquan; Israel, Karen
PATENT ASSIGNEE(S): Research Development Foundation, USA
SOURCE: U.S., 48 pp., Cont.-in-part of U.S. Ser. No. 404,001.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 4
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 6770672	B1	20040803	US 2000-502592	20000211
US 6417223	B1	20020709	US 1999-404001	19990923
CN 1706838	A	20051214	CN 2005-10003855	19990923
CA 2399802	A1	20010816	CA 2001-2399802	20010209
WO 2001058889	A1	20010816	WO 2001-US4168	20010209

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            HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,
            LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU,
            SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU,
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    JP 2004504268        T     20040212    JP 2001-558439          20010209
    NZ 520798            A     20040528    NZ 2001-520798          20010209
    CN 1529701           A     20040915    CN 2001-807536          20010209
    AU 2001236805        B2    20050714    AU 2001-236805          20010209
    RU 2263672           C2    20051110    RU 2002-124135          20010209
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    US 7312232           B2    20071225
    US 20040097431       A1    20040520    US 2003-695275          20031028
    US 7300954           B2    20071127
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    US 20080161349       A1    20080703    US 2007-928991          20071030
PRIORITY APPLN. INFO.:                       US 1998-101542P     P   19980923
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                                             CN 1999-812829      A3  19990923
                                             US 2000-502592      A   20000211
                                             WO 2001-US4168      W   20010209
                                             US 2001-8066        A3  20011105
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                                             US 2003-695275      A3  20031028
OTHER SOURCE(S):         MARPAT 141:174332
GI
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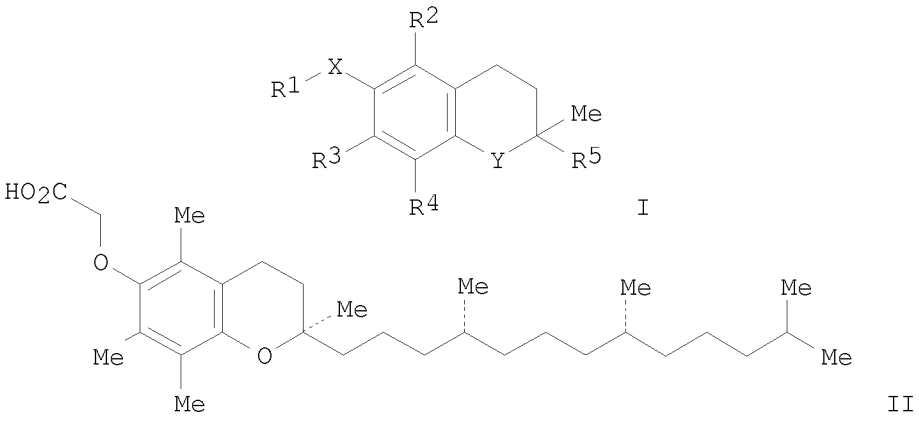


I

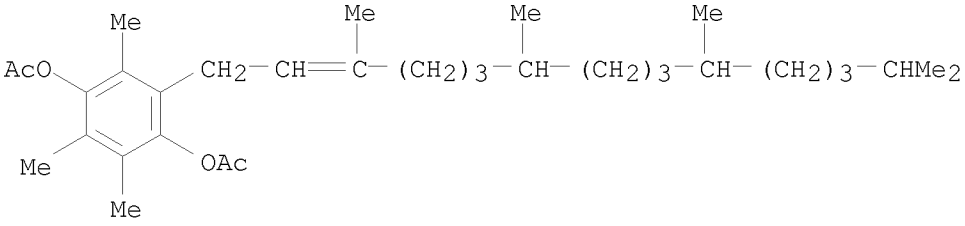
II

AB Chroman derivs., such as I [X = O, S, NR6; Y = O, NR6; R1 = carboxyalkyl, carboxyalkenyl, etc.; R2, R3, R4 = H, Me, alkyl, etc.; R5 = alkyl, alkenyl, etc.; R6 = H, alkyl], were prepared for use in antitumor pharmaceutical compns. for inducing apoptosis in a cell, particularly a cancer cell. Thus, α-tocopherol derivative II was prepared in 88% yield by a reaction of BrCH2CO2Me with (R,R,R)-α-tocopherol using NaOH in DMF. The prepared chromans were assayed for growth inhibitory and apoptotic activity against a variety of human cancer cell lines.

IT 85314-71-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of tocopherols, tocotrienols, other chroman and side chain derivs. for therapeutic use in prevention and treatment of cancer)

RN 85314-71-2 CAPLUS

CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)



REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 3 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2002:595501 CAPLUS

DOCUMENT NUMBER: 137:140656

TITLE: Preparation of tocopherols, tocotrienols, other chromans and side chain derivs. as potential antiproliferative and proapoptotic agents

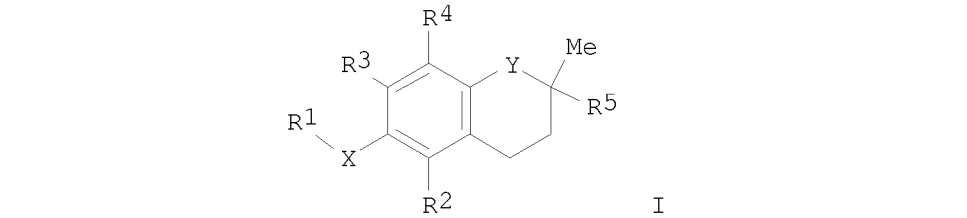
INVENTOR(S): Sanders, Bob G.; Kline, Kimberly; Yu, Weiping

PATENT ASSIGNEE(S): Research Development Foundation, USA
SOURCE: U.S. Pat. Appl. Publ., 44 pp., Cont.-in-part of U. S. Ser. No. 502,592.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 4
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20020107207	A1	20020808	US 2001-8066	20011105
US 6703384	B2	20040309		
US 6417223	B1	20020709	US 1999-404001	19990923
CN 1706838	A	20051214	CN 2005-10003855	19990923
US 6770672	B1	20040803	US 2000-502592	20000211
WO 2003039461	A2	20030515	WO 2002-US35147	20021101
WO 2003039461	A3	20031113		
W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
AU 2002353971	A1	20030519	AU 2002-353971	20021101
US 20040097431	A1	20040520	US 2003-695275	20031028
US 7300954	B2	20071127		
US 20080161349	A1	20080703	US 2007-928991	20071030

PRIORITY APPLN. INFO.:		
US 1998-101542P	P	19980923
US 1999-404001	A2	19990923
US 2000-502592	A2	20000211
CN 1999-812829	A3	19990923
US 2001-8066	A	20011105
WO 2002-US35147	W	20021101
US 2003-695275	A3	20031028

OTHER SOURCE(S): MARPAT 137:140656
GI



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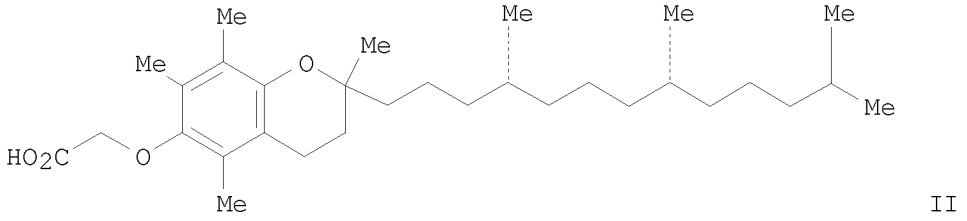


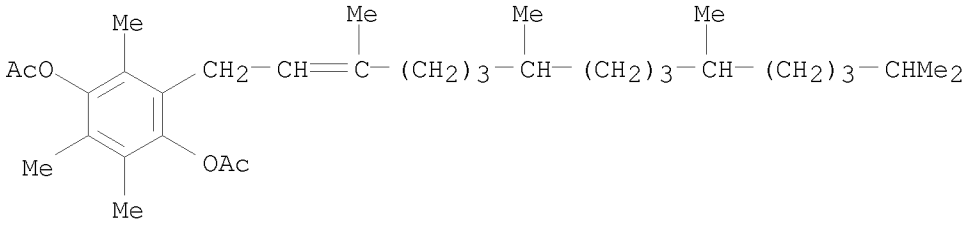
II

AB Derivs. of tocopherol, tocotrienol and other chromans of formula I (X and Y independently are oxygen, nitrogen or sulfur; when Y is nitrogen, nitrogen is substituted with R6 and R6 = H or Me; R1 = alkyl, alkenyl, alkynyl, aryl, heteroaryl, carboxylic acid, carboxylate, carboxamide, ester, thioamide, thiolacid, thiol ester, saccharide, alkoxy-linked saccharide, amine, sulfonate, sulfate, phosphate, alc., ethers or nitrites; R2, R3 = hydrogen or R4; R4 = Me, benzyl carboxylic acid, benzyl carboxylate, benzyl carboxamide, benzyl ester, saccharide or amine; and R5 = alkenyl) were prepared as antiproliferative and proapoptotic agents for the potential treatment of cell proliferative diseases. Thus, α-tocopherol was treated with Me bromoacetate and NaOH in N, N-dimethylformamide to give II. II showed effective growth inhibitory properties (apoptotic inducing) in a wide variety of human cancer cell lines, including breast, prostate, cervical, and ovarian cancers with EC50 values ranging from 1-20 μg/mL.

IT 85314-71-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of tocopherols, tocotrienols, other chromans and side chain derivs. as potential antiproliferative, proapoptotic agents for the treatment of cancer)

RN 85314-71-2 CAPLUS

CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)

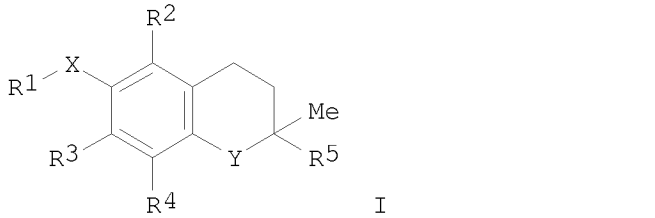


L11 ANSWER 4 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 2001:597976 CAPLUS
DOCUMENT NUMBER: 135:166941
TITLE: Preparation of tocopherols, tocotrienols, other chroman and side chain derivatives that induce cell apoptosis for therapeutic use as antiproliferative agents
INVENTOR(S): Sanders, Robert G.; Kline, Kimberly; Hurley, Laurence; Gardner, Robb; Menchaca, Marla; Yu, Weiping; Ramanan, Puthucode N.; Liu, Shenquan; Israel, Karen
PATENT ASSIGNEE(S): Research Development Foundation, USA
SOURCE: PCT Int. Appl., 120 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 4
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001058889	A1	20010816	WO 2001-US4168	20010209
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
US 6770672	B1	20040803	US 2000-502592	20000211
CA 2399802	A1	20010816	CA 2001-2399802	20010209
EP 1254130	A1	20021106	EP 2001-909008	20010209
EP 1254130	B1	20080102		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
JP 2004504268	T	20040212	JP 2001-558439	20010209
NZ 520798	A	20040528	NZ 2001-520798	20010209
AU 2001236805	B2	20050714	AU 2001-236805	20010209
RU 2263672	C2	20051110	RU 2002-124135	20010209
KR 847678	B1	20080723	KR 2002-710387	20020810

PRIORITY APPLN. INFO.:	US 2000-502592	A	20000211
	US 1998-101542P	P	19980923
	US 1999-404001	A2	19990923
	WO 2001-US4168	W	20010209

OTHER SOURCE(S): MARPAT 135:166941
GI



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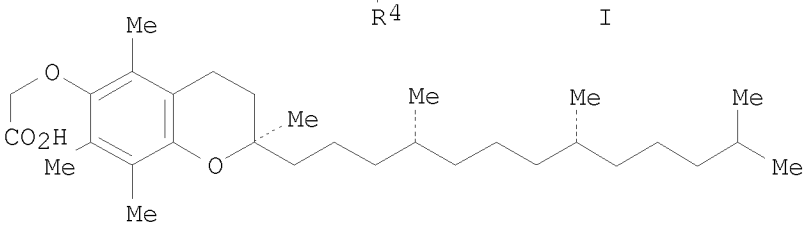


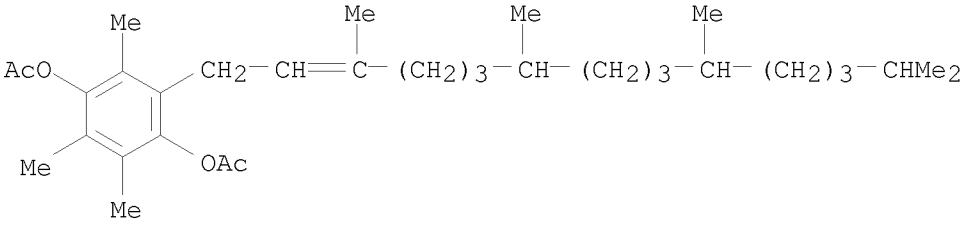
II

AB Tocopherol analogs, such as I [X = O, NH, S; Y = O, NH, S; R1 = alkyl, alkenyl, alkynyl, aryl, heteroaryl, carboxyl, carboxamide, thiocarboxyl, etc.; R2, R3, R4 = H, Me, benzyl, carboxyl, carboxamide, amine, saccharide; R5 = alkyl, alkenyl, alkynyl, aryl, heteroaryl, carboxyl, carboxamide], were prepared for pharmaceutical use as antiproliferative agents which induce cell apoptosis for treatment of cancers and diseases involving cell proliferation, such as autoimmune diseases, psoriasis, etc.. Thus, (R,R,R)-α-tocopherol derivative II was prepared in 88% yield by condensation of (R,R,R)-α-tocopherol and BrCH2CO2Me in DMF using NaOH followed by hydrolysis with 5 N HCl. The prepared tocopherol analogs were tested for their ability to induce apoptosis in a number of cancer cell lines, such as breast, cervical, colon, prostate, etc.

IT 85314-71-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of tocopherols, tocotrienols, other chromans that induce cell apoptosis for therapeutic use as antiproliferative agents)

RN 85314-71-2 CAPLUS

CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)

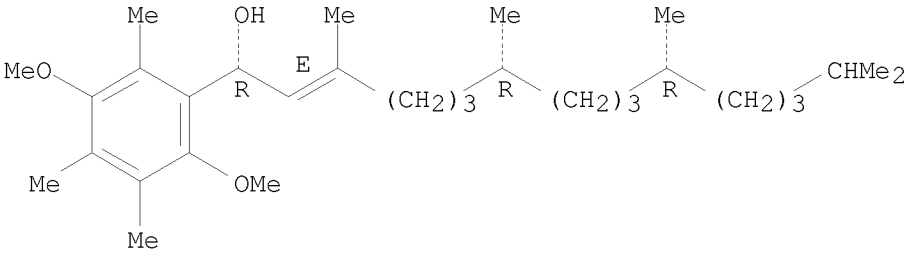


REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 5 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1991:6894 CAPLUS
DOCUMENT NUMBER: 114:6894

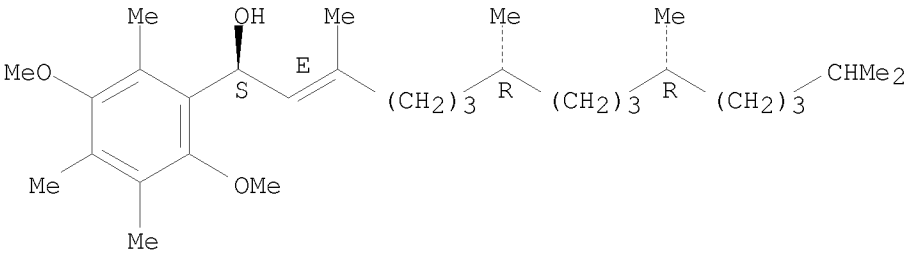
ORIGINAL REFERENCE NO.: 114:1359a,1362a
TITLE: Total synthesis of naturally occurring α-tocopherol. Part 5. Asymmetric alkylation and asymmetric epoxidation as means to introduce (R)-configuration at C(2) of the chroman moiety
AUTHOR(S): Huebscher, Josef; Barner, Richard
CORPORATE SOURCE: Zent. Forschungseinheiten, F. Hoffmann-La Roche A.-G., Basel, CH-4002, Switz.
SOURCE: Helvetica Chimica Acta (1990), 73(4), 1068-86
CODEN: HCACAV; ISSN: 0018-019X
DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 114:6894
AB Several variations of the title approaches were used in the stereoselective total synthesis of (2R,4'R,8'R)-α-tocopherol.
IT 130627-52-0P 130697-18-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 130627-52-0 CAPLUS
CN Benzenemethanol, 2,5-dimethoxy-3,4,6-trimethyl-α-(2,6,10,14-tetramethyl-1-pentadecenyl)-, [6R-[1E(R*),6R*,10R*]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.



RN 130697-18-6 CAPLUS
CN Benzenemethanol, 2,5-dimethoxy-3,4,6-trimethyl-α-(2,6,10,14-tetramethyl-1-pentadecenyl)-, [6R-[1E(S*),6R*,10R*]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.

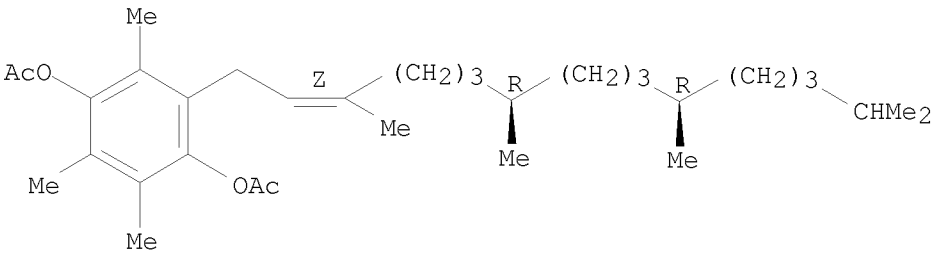


L11 ANSWER 6 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1984:497728 CAPLUS
DOCUMENT NUMBER: 101:97728
ORIGINAL REFERENCE NO.: 101:14875a,14878a
TITLE: Isolation and identification of some degradation products of tocopherol and its acetate
AUTHOR(S): Proksa, B.; Skoda, A.
CORPORATE SOURCE: Slovakofarma, Hlohovec, CS-92027, Czech.
SOURCE: Pharmazie (1984), 39(4), 279
CODEN: PHARAT; ISSN: 0031-7144
DOCUMENT TYPE: Journal
LANGUAGE: English
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Degradation products and byproducts of synthesis, I [39269-99-3], II [91432-36-9], III [91432-37-0], IV [91432-38-1], V [72657-56-8], and VI [91465-78-0], of tocopherol (VII) [59-02-9] and its acetate, VIII [1406-70-8], were identified by HPLC. Combinations of silica gel, LiChrosorb RP-18 and RP-8 columns were used and various mobile phases such as MeOH-H2O (98:2), 0.2% iso-PrOH in hexane, and 5 or 1% EtOAc in hexane. The compds. were detected by UV.
IT 91432-36-9
RL: ANST (Analytical study)
(tocopherol acetate degradation product, identification of, by HPLC)
RN 91432-36-9 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecenyl)-, diacetate, [R-[R*,R*-(Z)]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.

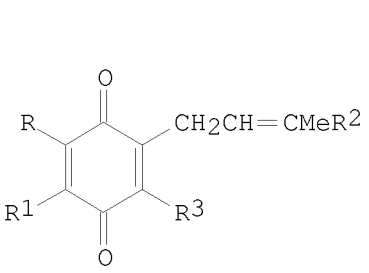


L11 ANSWER 7 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1984:423728 CAPLUS
DOCUMENT NUMBER: 101:23728
ORIGINAL REFERENCE NO.: 101:3765a,3768a
TITLE: Tocopherols and ubiquinones, their intermediate products, and their use
INVENTOR(S): Doetz, Karl Heinz
PATENT ASSIGNEE(S): Fed. Rep. Ger.
SOURCE: Ger. Offen., 27 pp.

CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 3221506	A1	19831208	DE 1982-3221506	19820607
JP 59001477	A	19840106	JP 1983-101570	19830607
JP 03039068	B	19910612		

PRIORITY APPLN. INFO.: DE 1982-3221506 A 19820607
OTHER SOURCE(S): CASREACT 101:23728; MARPAT 101:23728
GI



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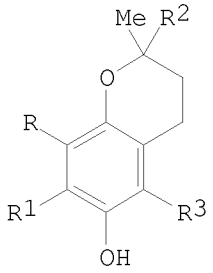

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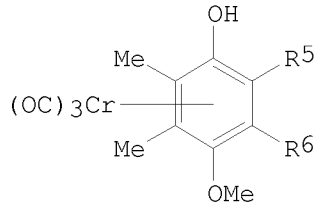


III

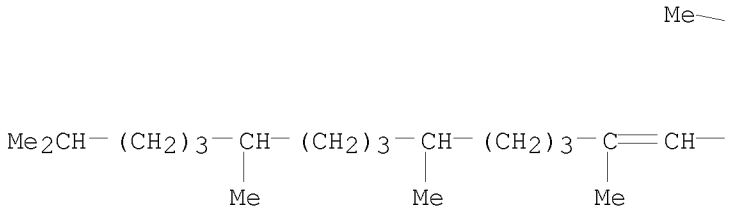
AB Tocopherolenes and ubiquinones I and II [R = H, Me, OMe; R1 = Me, OMe; R2 = {(CH2)3CHMe}3Me, {(CH2)2CH:CMe}3CH2R4; R3 = Me, Et, acyl, silyl; R4 = H, OH, alkoxycarbonyl] were prepared from carbonyl(alkenylcarbene)metal complexes and R3C.tplbond.CCH2CH:CMeR2. Thus Cr(CO)6 was treated with (E)-MeCLi:CHMe and Me3O+BF4- to give carbene (Z)-(CO)5Cr:C(OMe)CMe:CHMe, which cyclized with methylphytylacetylene to give arene-chromium complexes III [R5 = Me, R6 = (Z)-CH2CH:CMe(CH2CH2CH2CHMe)3Me; and vice versa]. III were decomplexed using 85 bar CO for 65 h at 80°, giving the corresponding arenes (IV). Bromination and cyclocondensation of IV [R5 = (Z)-CH2CH:CMe(CH2CH2CH2CHMe)3Me, R6 = Me] gave 96% Vitamin E.

IT 86993-68-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and decomplexation of, with carbon monoxide)

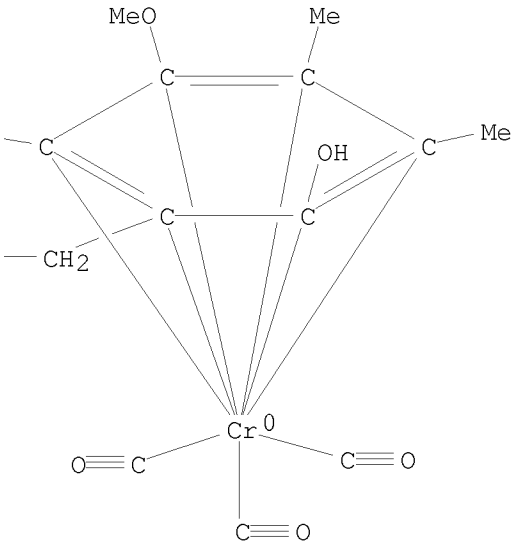
RN 86993-68-2 CAPLUS

CN Chromium, tricarbonyl[(1,2,3,4,5,6-η)-4-methoxy-2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecenyl)phenol]-, stereoisomer (9CI) (CA INDEX NAME)

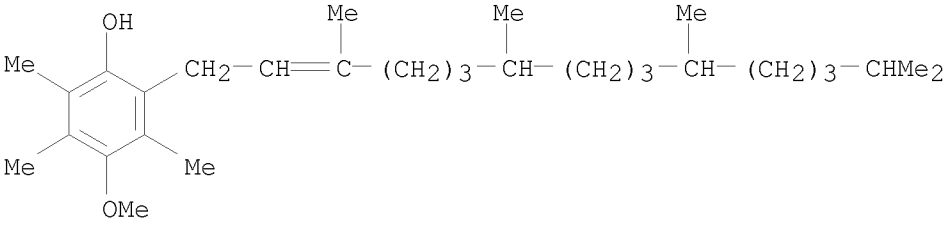
PAGE 1-A



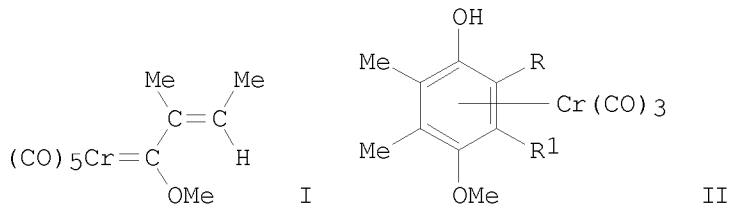
PAGE 1-B



IT 90510-40-0P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation, bromination, cyclization, and oxidation of)
RN 90510-40-0 CAPLUS
CN Phenol, 4-methoxy-2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecenyl)-
(9CI) (CA INDEX NAME)

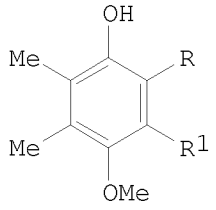


L11 ANSWER 8 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1983:540179 CAPLUS
DOCUMENT NUMBER: 99:140179
ORIGINAL REFERENCE NO.: 99:21545a,21548a
TITLE: Vitamin syntheses with carbene complexes. Part 5. A carbene complex route to vitamin E
AUTHOR(S): Doetz, Karl Heinz; Kuhn, Werner
CORPORATE SOURCE: Anorg. Chem. Inst., Tech. Univ. Muenchen, Garching, D-8046, Fed. Rep. Ger.
SOURCE: Angewandte Chemie (1983), 95(9), 750-1
CODEN: ANCEAD; ISSN: 0044-8249
DOCUMENT TYPE: Journal
LANGUAGE: German
GI

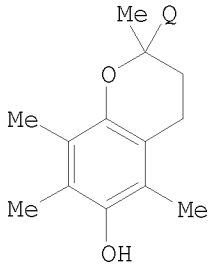


I

II



III



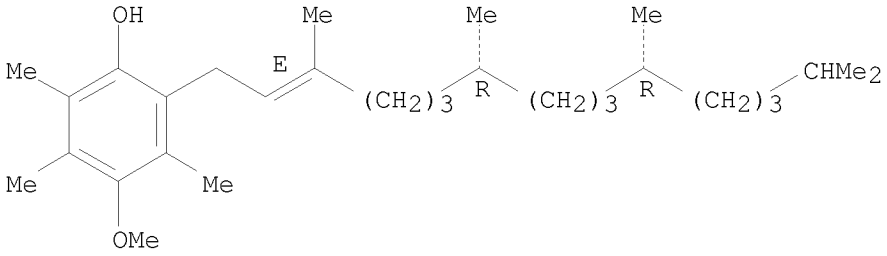
IV

AB I reacted with MeC.tplbond.CCH2CH:CMeQ [Q = [(CH2)3CHMe]2(CH2)3CHMe2] in Me3COMe ti give II [R = (E)-CH2CH:CMeQ; R1 = Me; R = Me, R1 = (E)-CH2CH:CMeQ] in 36 and 23% yields, resp., which in Et2O in an autoclave were treated with 80 bar CO at room temperature for 140 h to give quant. the resp. III, which were treated with BBr3 and then with H2O to give the de-O-methylated derivative of III (R = CH2CH2CMeBrQ, R1 = Me), cyclization of

which in the presence of $ZnCl_2$ gave α-tocopherol (IV).

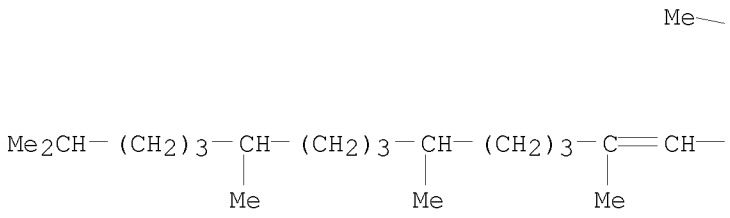
IT 86993-70-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and bromination-demethylation of)
RN 86993-70-6 CAPLUS
CN Phenol, 4-methoxy-2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecenyl)-, [R-[R*,R*-(E)]]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry as shown.

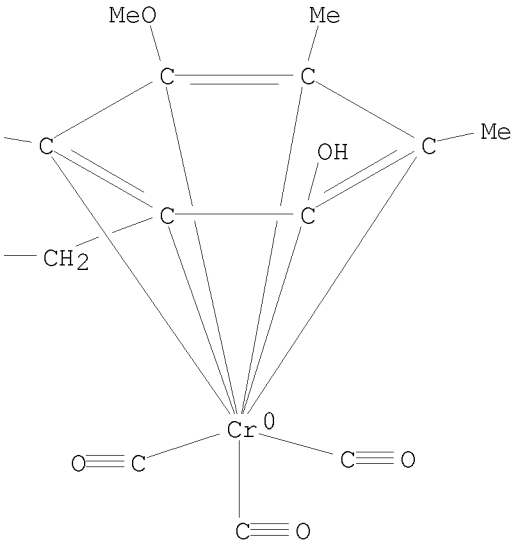


IT 86993-68-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and decomposition of)
RN 86993-68-2 CAPLUS
CN Chromium, tricarbonyl[(1,2,3,4,5,6-η)-4-methoxy-2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecenyl)phenol]-, stereoisomer (9CI) (CA INDEX NAME)

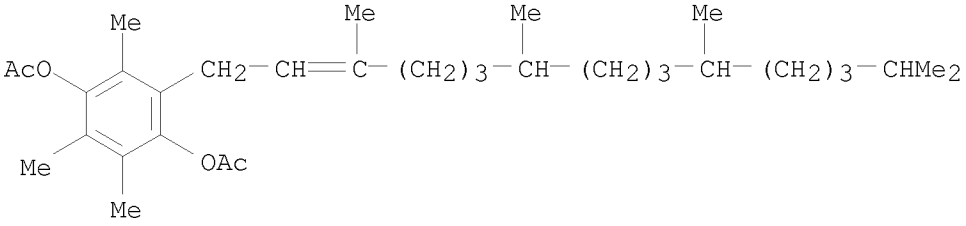
PAGE 1-A



PAGE 1-B



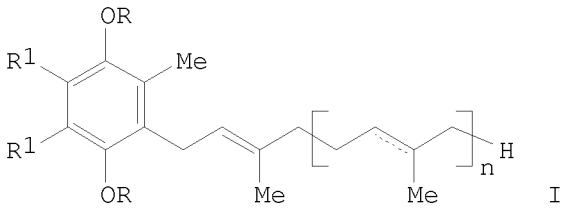
L11 ANSWER 9 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1983:160971 CAPLUS
DOCUMENT NUMBER: 98:160971
ORIGINAL REFERENCE NO.: 98:24435a,24438a
TITLE: Synthesis of vitamin E acetate
AUTHOR(S): Shchegolev, A. A.; Sarycheva, I. K.; Kochetova, E. V.; Mosolova, O. V.; Kulish, M. A.; Evstigneeva, R. P.
CORPORATE SOURCE: Inst. Tonk. Khim. Tekhnol., Moscow, USSR
SOURCE: Khimiko-Farmatsevticheskii Zhurnal (1983), 17(1), 92-4
CODEN: KHFZAN; ISSN: 0023-1134
DOCUMENT TYPE: Journal
LANGUAGE: Russian
OTHER SOURCE(S): CASREACT 98:160971
AB Vitamin E acetate was prepared in 92% yield by cyclocondensation of trimethylhydroquinone with isophytol 30 min in refluxing AcOH containing ZnCl2, followed by heating with Ac2O 30 min at 125-130°.
IT 85314-71-2P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 85314-71-2 CAPLUS
CN 1,4-Benzenediol, 2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecen-1-yl)-, 1,4-diacetate (CA INDEX NAME)



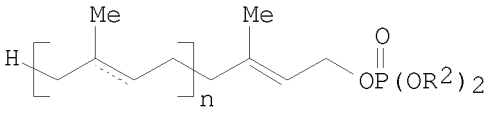
L11 ANSWER 10 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1983:34816 CAPLUS
DOCUMENT NUMBER: 98:34816
ORIGINAL REFERENCE NO.: 98:5453a,5456a
TITLE: Hydroquinone derivatives
PATENT ASSIGNEE(S): Kuraray Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 57095932	A	19820615	JP 1980-172272	19801205

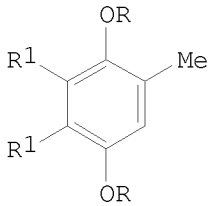
PRIORITY APPLN. INFO.: JP 1980-172272 19801205
GI



I



II

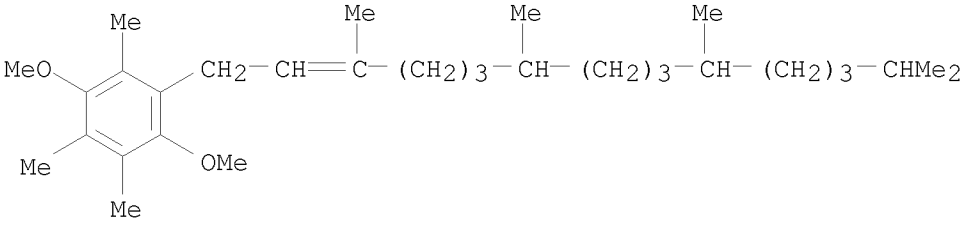


III

AB Hydroquinone derivs. I [R, R1, n, bond = Me, CH:CHCH:CH(R1R1), 1, double; Me, CH:CHCH:CH (R1R1), 0, –; MeOCH2CH2OCH2, CH:CHCH:CH (R1R1), 3, single; MeOCH2, CH:CHCH:CH (R1R1), 3, double; Me, Me, 3, single; MeOCH2CH2OCH2, MeO, 8, double; MeOCH2CH2OCH2, MeO, 8, double; MeOCH2CH2OCH2, MeO, 9, double] were prepared by reaction of II [R2 = (substituted) Ph with III at -80° to 0° in the presence of Lewis acids. Thus, a mixture of II (n = 1, double bond, R2 = Ph) 10, III (R = Me, R1R1 = CH:CHCH:CH) 10, and BF3-Et2O 10 mmol in CH2Cl2 was kept 4 h at -78° to give 25% I (R = Me, R1R1 = CH:CHCH:CH, n = 1, double bond).

IT 84113-82-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 84113-82-6 CAPLUS
CN Benzene, 1,4-dimethoxy-2,3,5-trimethyl-6-(3,7,11,15-tetramethyl-2-hexadecenyl)- (9CI) (CA INDEX NAME)



L11 ANSWER 11 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1965:498219 CAPLUS
DOCUMENT NUMBER: 63:98219
ORIGINAL REFERENCE NO.: 63:18038f-h,18039a-h,18040a-h,18041a-g
TITLE: Synthesis of substituted piperidine derivatives
PATENT ASSIGNEE(S): E. Merck A.-G.
SOURCE: 42 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
NL 6413199		19650608	NL 1964-13199	19641112
BE 656720			BE	
GB 1039450			GB	
PRIORITY APPLN. INFO.:			DE	19631207

AB The title compds. I, in which Z is S or (CH2)n (n is 1, 2, or 3), dehydration products of I, and quaternary salts and N-oxides thereof, are prepared by various standard methods, and are useful as narcotic, tranquilizing, sedative, hypnotic, thymoleptic, spasmolytic, and antihistaminic agents, and in some cases as stimulating or analeptic agents. Thus, to a mixture of 48.6 g. Mg in 50 ml. dry tetrahydrofuran (THF) is added with stirring a small amount of iodine and 5 g. EtBr, followed by a solution of 267 g. 4-chloro-N-methylpiperidine (II) in 450 ml. THF at 50-66°, and the mixture is refluxed 1 hr. and cooled to room temperature To this mixture is added with stirring a solution of 222 g. 2-phenyl-l-tetralone (III) in 500 ml. THF. The mixture is stirred 1 hr., kept overnight, and worked up to yield 65% recovered III and 70 g. 1-hydroxy-l-(N-methyl-4-piperidyl)- 2-phenyltetralin (IV), m.p. 115-16° (EtOH-H2O). Similarly are prepared, starting with the following 2-(substituted phenyl)-ltetralones (V), the following 1-hydroxy-l-(N-methyl-4-piperidyl)2-(substituted phenyl)tetralins (VI) (substituent, m.p. V, and m.p. VI given): o-Cl, 71°, 137-9°; p-Cl, 106°, 128-30° (compound with HCl and H2O); p-Br, 116°, 130-6° (decomposition) (compound with HCl and 2H2O); from 2-phenyl-6-methoxy-l-tetralone, m.p. 189°, 1-hydroxy-l-(N-methyl-4-piperidyl)-2-phenyl-6-methoxytetralin, b0.5 220-5°, Rf 0.55 (thin layer chromatography, details are given), was obtained. Also are prepared the following VI: o-Me, m.p. 146°; m-Me; p-Me, m-Cl; o-F; p-F; 3',4'di-Cl; 2',4'-di-Cl; o-OMe; m-OMe; p-OMe; 3',4'-di-OMe; 3',4',5'-tri-OMe; 3',4'-methylenedioxy; p-OEt; p-OBu; p-SMe; m-CF3; and p-CF3; the following 1-hydroxy-l-(N-methyl-4-piperidyl)-2-phenyl-substituted tetralins, substituent given: 5-Me; 5-Cl; 5-F; 6-Cl; 7-Br;

7-OMe; and 1-hydroxy-l-(N-methyl-4-piperidyi)-2-(p-methoxyphenyl)-6-methoxytetralin; and the following 1-hydroxy-l-(N-substituted 4-piperidyl)-2-phenyltetralins, substituent given: Et; Pr; iso-Pr; Bu; and further 1-hydroxy-l-(N-ethyl-4-piperidyl)-2-(o-tolyl)tetralin; and 1-hydroxy-l-(N-benzyl-4-piperidyl)-2-phenyl-5-methyltetralin. A solution of 32.15 g. IV in 48 ml. 15% HCl in iso-PrOH is refluxed 1 hr. to yield 25 g. 1-(N-methyl-6-piperidyl)-2-phenyl-3,4-dihydronaphthalene (VII).HCl, m.p. 258-62°; from the iso-PrOH solution, 6.3 g. VII (free base), m.p. 118-19° (EtOH-H2O), is isolated. From VII and MeI is prepared VII methiodide, m.p. 202-3° (EtOH-Et2O); from VII and benzyl chloride, VII benzochloride, m.p. 106-7° (acetone-Et2O). VII is also prepared with 92% yield from IV in 0.1N HCl (1 hr. at 90-100°). Similarly are prepared the following 1-(N-methyl-4-piperidyl)-2-substituted-phenyl-3,4-dihydronaphthalenes (VIII) (substituent and m.p. given): o-Cl, 125-6°; p-Cl, 280-4° (with HCl); p-Br, 160-2°; and 6-methoxy-l-(N-methyl-4-piperidyl)-2-phenyl-3,4-dihydronaphthalene. HCl salt m. 239-40°. VII is also prepared by boiling for 2 hrs. the decomposed (with acid) Grignard solution, used for the preparation of IV; similarly
are prepared, starting with the following substituted 2-phenyl-l-tetralones (IX), the following substituted 1-(N-methyl-4-piperidyl)-2-phenyl-3,4-dihydronaphthalenes (X) (substituent, m.p. IX, and m.p. X given): 7-Br, 103-5°, 11920°; 7-Cl, 91°, 285-7° (with HBr); 5-Cl, 113-14°, 279-82°, (with HBr); and 6-methoxy-2-(p-methoxyphenyl)-l-(N-methyl-4-piperidyl)-3,4-dihydronaphthalene-HCl, m.p. 249-52° (from 6-methoxy-2-(p-methoxyphenyl)-1-tetralone, m.p. 127°). Similarly are prepared the following 1-(N-substituted-4-piperidyl)-2phenyl-3,4-dihydronaphthalenes (substituent given): Pr; iso-Pr; Bu; iso-Bu; sec-Bu; and tert-Bu; the following VIII, substituent given: o-Me; m-Me; p-Me; m-Cl; o-F; m-F; p-F; 2',4'-di-Cl; 3',4'-di-OMe; p-SMe; p-SEt; m-CF3; and p-CF3; and the following X: 6-Cl; 5-Me; 5,8-di-Me; 7-OMe, 7-OEt; 5-F; 5-OMe; 6-Me; 7-Me; 5,7-di-Cl; the following 3,4-dihydronaphthalenes: 1-(N-ethyl-4-piperidyl)-2-(o-tolyl); 1-(N-butyl-4-piperidyl)-2-(m-chlorophenyl); 7-bromo-1-(N-methyl-4-piperidyl); 2-(p-bromophenyl); 1-(N-ethyl-4-piperidyl)-5-chloro-2-phenyland 2-methyl-l-(N-methyl-4-piperidylidene)-2-phenyltetralin and the corresponding N-benzyl compound; 2-ethyl-l-(N-methyl-4piperidylidene)-2-phenyltetralin and the corresponding N-benzyl compound; 7-chloro-2-methyl-l-(N-methyl-4-piperidylidene)-2phenyltetralin; and 2-ethyl-2-(o-chlorophenyl)-l-(N-methyl-4piperidylidene)tetralin. VII can be prepared with nearly 100% yield from IV with concentrated HCl; with concentrated HCl and glacial AcOH; in toluene with p-toluenesulfonic acid, or P2O5; with POCl3; in CHCl3, with AcCl; in iso-PrOH with 40% HBr; with KHSO4; or with C2H2O4.2H2O; details are given; IV and VII can be identified (thin layer chromatography), having Rf 0.35 and 0.7 respectively. From 5.5 g. Mg, 30 g. II, and 24.5 g. 2methyl-2-phenyl-l-indanone (XI) is, according to the method used for IV, prepared 29.5 g. 1-hydroxy-l-(N-methyl-4-piperidyl)2-methyl-2-phenylindan (XII), m.p. 205° [dimethylformamide (DMF)-H2O]. Similarly are prepared, starting with the following substituted 2-phenyl-l-indanones (XIII), the following substituted 1-hydroxy-1-(N-methyl-4-piperidyl)-2-phenylindans (XIV) (substituent, phys. consts. of XIII and XIV given): 2-Et, -, b0.5 226-8°; 2-Bu, b0.05 158-60°, b0.02 220-5°; 2-benzyl, m.p. 145°, m.p. 248-51° (DMF-EtOH); and the following substituted 1-hydroxy-2-methyl-l-(N-methyl-4-piperidyl)indans (substituent given): 2-(o-chlorophenyl); 2-(m-chlorophenyl); 2-(p-chlorophenyl); 4-Cl-2-Ph; 6-OMe-2-Ph; 4-Cl-2-(o-chlorophenyl); 6-OMe-2-(o-tolyl); and

1-(N-ethyl-4-piperidyl)-1-hydroxy-2-methyl-2-phenylindan; and 2-(o-tolyl)-1-hydroxy-2-methyl-1-(Nbenzyl-4-piperidyl)indan (XIVa). A solution of 150 g. XII in 200 ml. iso-PrOH and 500 ml. 12% HCl in iso-PrOH is refluxed 1 hr. to yield 140 g. 2-methyl-1-(N-methyl-4-piperidylindene)-2-phenylindan (XV).HCl, m.p. 245° (iso-PrOH). A mixture of 27 g. XII and 54 g. KHSO4 is heated 2 hrs. at 180° and 15 min. at 240°, and worked up to yield 22 g. XV, b0.2 203-4°. Similarly are prepared the following substituted 1-(N-methyl-4-piperidylidene)-2-phenylindans (substituent and phys. consts. given): 2Et, b0.5 205-7°; 2-Bu, b1-2 225-8°; 2-benzyl (XVI), b0.05 21015°; XVI p-toluenesulfonate, m.p. 247-8°. According to the method used for XII, is prepared racemic 1-hydroxy-6-methyl-2-methyl-1-(N-methyl-4-piperidyl)-2-phenylindan (XVII), b1 2314°, m.p. 165-73° (DMF-H2O), Rf 0.32 and 0.48 (from 6-OMeXI, m.p. 65°). A mixture of 35 g. XVII and 200 ml. freshly distilled POCl3 is heated 1.5 hrs. at 50-90° and worked up to yield 31 g. 6-methoxy-2-methyl-1-(N-methyl-4-piperidylidene)-2-phenylindan (XVIII), b0.1 229-31; to 31 g. XVIII, dissolved in 105 ml. 2N AcOH is added a solution of 6 g. NaCl in 30 ml. H2O to yield 27.5 g. XVIII.HCl.H2O, m.p. 149-51° (EtOH-H2O), Rf 0.55. To 2.5 g. of a Mg-Cu alloy (containing 12.75% Cu) in 10 ml. dry Et2O is added 0.5 ml. MeI, 7.5 g. Mg, 20 ml. THF, and drop-wise a solution of 53.5 g. II in 180 ml. Et2O, and the mixture is boiled several hrs. and cooled. To this mixture is added dropwise with stirring a solution of 47.3 g. 2-methyl-III in 400 ml. Et2O, and the mixture is stirred 20 hrs. to yield 2-methyl-IV, b0.8 214-5°; 2methyl-IV.HCl, m.p. 250° (EtOH-Et2O). Similarly are prepared 1-(N-ethyl-4-piperidyl)-1-hydroxy-2-methyl-2-phenyltetralin, and the corresponding N-benzyl compound To a mixture of 92 g. 2phenyl-2,3-dihydrothionaphthen-3-one and K tert-butylate (prepared from 22 g. K) in 1.5 l. C6H6 is added 110 g. MeI in 1 l. C6H6 at 20-30°. The mixture is stirred 2 hrs. at room temperature and refluxed for 3 hrs., to yield 90.5 g. of a mixture (XIX) of 2-methyl-2-phenyl-2,3-dihydrothionaphthen-3-one (XX) and 1-methoxy-2-phenylthionaphthene; XIX b0.1 160-5°. From XIX in iso-PrOH, 40-5 g. pure XX, m.p. 96-7°, is isolated. According to the methods used for IV, 72 g. XX is converted into 71.5 g. 3-hydroxy-2methyl-3-(N-methyl-4-piperidyl)-2-phenyl-2,3-dihydrothionaphthene (XXI) (mixture of α- and β-racemate). This mixture is recrystd. from EtOAc and refluxed 1 hr. with 300 ml. cyclohexane, and filtered hot. The residue is recrystd. to yield 28 g. XXI (αracemate), m.p. 208-10° (iso-PrOH), Rf 0.3-0.4. From the cyclohexane solution, 15 g. XXI (β-racemate), m.p. 155-7° (isoPrOH), Rf 0.6-0.7 is isolated. XXI can also be prepared from crude XIX. Similarly are prepared the following substituted 3-hydroxy-3-(N-methyl-4-piperidyl)-2,3-dihydrothionaphthenes (substituents given): 2-Et-2-Ph; 2-Me-2-(p-chlorophenyl); 2-Me-2(m-chlorophenyl); 6-Cl-2,4-di-Me-2-Ph; and 6-OEt-2-Me-2-Ph. To a solution of 34 g. XXI in 200 ml. iso-PrOH is added 40% aqueous HBr till pH 1-2. The mixture is refluxed 4 hrs. to yield 32 g. 2methyl-3-(N-methyl-4-piperidylidene)-2-phenyl-2,3-dihydrothionaphthene (XXII).HBr, m.p. 248-52° (EtOH); XXII.HCl m. 255-6°. From 40 g. N-butyl-4-chloropiperidine (b100 139-46°) is prepared 19 g. 1-(N-butyl-4-piperidyl)-1-hydroxy-2-methyl-2-phenylindan (mixture of racemates, Rf 0.6 and 0.75), which is converted in acidic solution into 17 g. 1-(N-butyl-4-piperidylidene)-2-methyl-2-phenylindan (XXIII), b0.05 190-8°; XXIII.HBr m. 231-2° (iso-PrOH-H2O). Similarly are prepared (from N-benzyl-4-chloropiperidine, b10 153-7°) 1-(N-benzyl-4-piperidyl)-1-hydroxy-2-methyl-2-phenylindan (XXIV), b0.1 235-50°; XXIV, α-racemate, m.p. 83-4° (EtOH), Rf 0.6;

XXIV, β-racemate, Rf 0.85, was not isolated pure; 1-(N-benzyl-4-piperidyl)-1-hy-droxy-2-phenyltetralin (XXV); XXV, α-racemate, compound with C2H2O4, m.p. 177-9° (EtOH-Et2O); and the following substituted 1-(N-benzyl-4-piperidyl)-1-hydroxytetralin (substituents given): 2-(o-fluorophenyl); 2-(o-tolyl); 2-(p-methoxyphenyl); and 2Ph-5-F. XXIV is converted in iso-PrOH-HBr into 1-(Nbenzyl-4-piperidylidene)-2-methyl-2-phenylindan XXVI.HBr m. 219-20° (acetone); similarly, XXV (α-racemate) yields 90% 1-(N-benzyl-4-piperidyl)-2-phenyl-3,4-dihydronaphthalene-HBr, m.p. 252-4°. To a solution of 12.6 g. XXV (α-racemate-C2H2O4) in 200 ml. MeOH is added 10 g. Pd-C and the mixture is hydrogenated 2 hrs. at 20°/6 atmospheric H to yield 8 g. 1-hydroxy-1-(4-piperi-dyl)-2-phenyltetralin (XXVII).HCl, m.p. 262-3°, Rf 0.1. Similarly are prepared (from XXIV) 1-(4-piperidyl)-2-methyl-2-phenyl-4-indanol (XXVIII), Rf 0.15; and the following substituted 1hydroxy-1-(4-piperidyl)tetralins (substituent given): 2-(o-toluyl), 2-(o-fluorophenyl); 2-Me-2-Ph; and 5-Me-2-Ph. From 5.5 g. XXVII.HCl in iso-PrOH-HBr is obtained 5 g. 1-(4-piperidyl)-2-phenyl-3,4-dihydronaphthalene (XXIX).HCl, m.p. 274-6° (isoPrOH-Et2O); XXIX, m.p. 94-6° (diisopropyl ether). Similarly are prepared from the corresponding N-benzylcarbinols the following substituted 1-(4-piperidyl)-3,4-dihydronaphthalenes (substituent given): 2-(o-tolyl); 2-(p-methoxyphenyl); 5-F-2-Ph; and 5-Me-2-Ph. A mixture of 1 g. XXIX, 0.33 g. formic acid, and 0.34 g. 40% formaldehyde solution is heated 1 hr. at 70° to yield 0.8 g. VII; similarly, 1-(4-piperidylidene)-2-methyl-2-phenylindan (XXX) is converted into XV. A mixture of 2.9 g. XXIX, 30 ml. C6H6, and 10 g. EtBr is refluxed 14 hrs., and the cooled mixture extracted with NH4OH. The C6H6 layer is evaporated and the residue is heated 2 hrs. at 80° with 10 ml. Ac2O and worked up to yield 2.5 g. 1-(N-ethyl-4-piperidyl)-2-phenyl-3,4-dihydronaphthalene-HCl (XXXI), m.p. 277-8° (H2O). Similarly are prepared 1-(N-benzyl-4-piperidyl)-2-phenyl-3,4-dihydronaphthalene (from XXIX) and 1-(N-butyl-4-piperidylidene)-2-methyl-2-phenylindan (XXXII) (from XXX). To a solution of 14.3 g. XV in 50 ml. dry C6H6 is added dropwise 16.3 g. chloroformic acid Et ester, and the mixture is heated 1.5 hrs. at 40-50° to yield 1-(N-carbethoxy-4-piperidylidene) 2-methyl-2-phenylindan, which is boiled 10 hrs. with a solution of 8.4 g. KOH in 9 ml. H2O and 60 g. diethylene glycol mono Et ether to yield 12 g. XXX.HNO3, m.p. 188-9° (decomposition). Similarly are prepared XXIX (from VII); and XXX-HNO3 from XXXII and from XXVI. To a solution of 5 g. VII in 80 ml. EtOH is added with stirring 10 g. 30% H2O2; after 20 hrs. at 25°, the mixture is heated 3 hrs. at 60°, and the excess H2O2 is decomposed with a trace PtO2 to yield 4.8 g. 1-(N-methyl-4-piperidyl)-2-phenyl-3,4-dihydronaphthalene N-oxide-H2O, m.p. 140-4°. Similarly is prepared 2-methyl-1-(N-methyl-4piperidylidene)-2-phenyltetralin N-oxide-0.5 H2O, m.p. 227-8° (decomposition) (acetone-H2O) (from 2-methyl-IV via dehydration and oxidation). To a solution of 2 g. BrCN in 10 ml. C6H6 is added dropwise a solution of 2 g. VII in 10 ml. C6H6, the mixture is kept overnight and heated 2 hrs. at 60-70° to yield 0.9 g. XXIX. A mixture of 2 g. XXIX, 40 ml. EtOH, and 15 ml. acetaldehyde is hydrogenated with H and Raney Ni; the mixture is filtered and evaporated and the residue is heated 1 hr. at 80° with 10 ml. Ac2O to yield 1.5 g. XXXI. According to the method used for the preparation of XXX, 10 g. XXII is converted into 8 g. 2-methyl-3-(4-piperidylidene)-2-phenyl-2,3-dihydrothionaphthene-HCl, m.p. 237-8° (EtOH). Similarly, XII is converted into XXVIII. According to the method used for the preparation of IV, the following substituted 5-hydroxy-5-(N-methyl-4-piperidyl)benzosuberans are prepared (substituent given): 6-Ph; 6-Me-6-Ph; 6-(m-chlorophenyl);

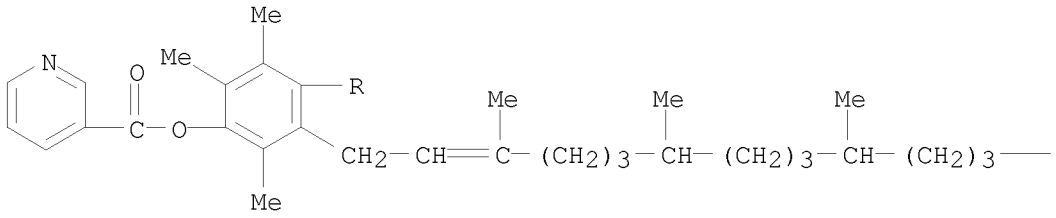
6-(o-tolyl); 1-Cl-6-Ph; 3-Br-6-Ph; 1-Me-6-(o-chlorophenyl); and 9.-Cl-6-Me-6-(o-tolyl); and the following 5-hydroxy- 5: (N-substituted-4-piperidy-1)-6-phenylbenzosuberans (substituent given): Et; benzyl (XXXIII). By catalytic debenzylation, XXXIII is converted into 5-hydroxy-5-(4-piperidyl)6-phenylbenzosuberan, and XIVa into 1-hydroxy-2-methyl-l-(4piperidyl)-2-(o-toluyl)indan. By already described methods were prepared the following 5-(N-substituted-4-piperidyl)-6-phenyl-5,6-dehydrobenzosuberans (substituent given): Me; Et; Bu; benzyl; the following 6-methyl-5-(N-substituted-4-piperidylidene)-6-phenylbenzosuberans (substituent given): Me; Et; Bu; benzyl; 6-ethyl-5-(N-methyl-4-piperidylidene)-6-phenylbenzosuberan; the following 6-(substituted phenyl)-5-(N-methyl-4piperidyl)-5,6-dehydrobenzosuberans (substituent given): o-Cl; m-Cl; p-Cl; p-Br; p-OMe; p-SMe; o-Me; m-Me; p-Me; and 6-(o-tolyl) [and the corresponding 6-(p-tolyl)]-5-(N-benzyl-4piperidyl)-5,6-dehydrobenzosuberan; the following substituted 5-(N-methyl-4-piperidyl)-6-phenyl-5,6-dehydrobenzosuberans (substituent given): 1-Cl; 3-Cl; 3-Br; 1-Me; 3-Me; 3-iso-Pr; 2-OEt-3-OMe; 1-OEt; 2,3-di-OMe; 1-OMe; 3-OMe; 2,3methylenedioxy; the following substituted 5-(N-methyl-4piperidylidene)benzosuberans (substituents given): 3-Br-6-Me-6-Ph; 6-(o-chlorophenyl)-6-Me; 1-Cl-6-(p-methoxyphenyl)-6Me; and 6-methyl (and the corresponding 6-ethyl)-5-(N-benzyl-4-piperidylidene)-6-phenylbenzosuberan; the following substituted 1-(N-ethyl-4-piperidylidene)indans: 2-Me-2-Ph; 4-Cl-2-(o-chlorophenyl); the following 1-(N-benzyl-4-piperidylidene)indans: 2-Me-2-Ph; 2-Me-2-(p-methoxyphenyl); the following 1-(N-methyl-4-piperidylidene)indans: 2-Me-2-(o-chlorophenyl); 2-Me-2-(m-chlorophenyl); 2-Et-6-Br-2-Ph; and 2-methyl-l-(N-propyl-4-piperidylidene)-2-phenylindan; the following 3-(Nsubstituted -4-piperidylidene) - 2 - methyl - 2 - phenyl - 2, 3 - dihydrothionaphthenes: Et; Pr; Bu; the following 3-(N-substituted-4piperidylidene)-2-methyl-2-(o-tolyl)- 2,3 - dihydrothionaphthenes: Me; Et; and the following substituted 3-(N-methyl-4-piperidylidene)-2,3-dihydrothionaphthenes: 2-Et-2-Ph; 2-Me-2-(o-chlorophenyl); 2-Me-2-(p-methoxyphenyl); 6-Cl-2,3-di-Me-2-Ph; 6-OEt-2-Me-2-Ph; 2-Me-2-(m-tolyl); 2-Me-2-(p-tolyl); 5-Cl-2,7di-Me-2-Ph; 6-Cl-2-Me-2-Ph; 6-OMe-2-Me-2-Ph; 5-Br-2-Me-2-Ph. By catalytic debenzylation, followed by dehydration were prepared the following 2-methyl-l-(4-piperidylidene)indans: 2-Ph; 2-(p-methoxyphenyl); 2-methyl (and the corresponding 2-ethyl)1-(4-piperidylidene)-2-phenyltetralin; 6-methyl (and the corresponding 6-ethyl)-5-(4-piperidylidene)-6-phenylbenzosuberan. The following salts of VII were prepared: VII.HBr, m.p. 270-2° (EtOH); VII.H3PO4.H2O, m.p. 227-35° (H2O); VII.H2SO4, m.p. 180-2° (iso-PrOH); VII-citric acid-H2O, m.p. 95-9° (decomposition) (iso-PrOH); VII-tartaric acid, m.p. 176-7° (iso-PrOH).

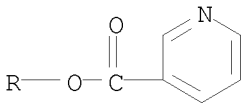
IT 4498-47-9P, Nicotinic acid, trimethylphytyl-p-phenylene ester
RL: PREP (Preparation)
(preparation of)

RN 4498-47-9 CAPLUS

CN Nicotinic acid, trimethylphytyl-p-phenylene ester (7CI, 8CI) (CA INDEX NAME)

PAGE 1-A





PAGE 1-B

— $CHMe_2$

L11 ANSWER 12 OF 12 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1965:498218 CAPLUS
DOCUMENT NUMBER: 63:98218
ORIGINAL REFERENCE NO.: 63:18038f
TITLE: 2,5,6-Trimethyl-3-phytyl-1,4-hydroquinone dinicotinate
INVENTOR(S): Nakano, Hiroshi; Morimoto, Akira; Yoshimitsu, Hideyuki
PATENT ASSIGNEE(S): Fujisawa Pharmaceutical Co., Ltd.
SOURCE: 2 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 40017022	B4	19650803	JP	19630520

PRIORITY APPLN. INFO.: JP 19630520

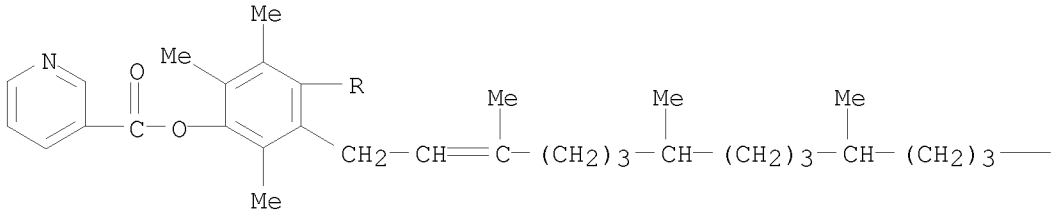
AB A mixture of 9.8 g. nicotinic acid and 60 cc. $SOCl_2$ is refluxed, 40 cc. pyridine added, cooled at 0°, a solution of 1.973 g. α-tocopherylhydroquinone in 20 cc. pyridine is added, and the whole stirred at 0° for 3 hrs. in a N stream in a dark place to give 1.208 g. title compound, m. 89-92° (hexane), which has vitamin E and nicotinic acid-like activities.

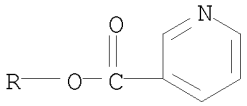
IT 4498-47-9P, Hydroquinone, trimethylphytyl-, dinicotinate
RL: PREP (Preparation)
(preparation of)

RN 4498-47-9 CAPLUS

CN Nicotinic acid, trimethylphytyl-p-phenylene ester (7CI, 8CI) (CA INDEX NAME)

PAGE 1-A





PAGE 1-B

— $CHMe_2$

=> log h

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	123.44	395.41

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
CA SUBSCRIBER PRICE	-16.00	-16.00

SESSION WILL BE HELD FOR 120 MINUTES
STN INTERNATIONAL SESSION SUSPENDED AT 17:47:08 ON 05 AUG 2008